

Fig. 5. Comparison of magnetization versus applied field for Ni metal (\bullet) (left scale) and for Nipillared α -ZrP (\bullet) (right scale) after calcination.

atoms are about 5 Å from the Ni central layer, and thus they are not directly connected to the central layer.

Magnetic susceptibility measurements were carried out on several samples of $Zr(PO_4)_2$ -Ni₄(OH)₅(C₂H₃O₂)·2H₂O and $Zr(PO_4)_2Ni_4O_3$ by the Faraday method at a field of 8 kG over a temperature range of 10 to 300 K. Quantitative samples (20 to 40 mg) were contained in carefully dried capsules (Kel-F), the susceptibilities of which were measured in separate runs and corrected for core diamagnetism and container contributions. The composite that formed at room temperature is paramagnetic, as shown by the data in Fig. 3. The magnetic moment μ_{eff} per Ni is 2.997 Bohr magnetons, which is slightly higher than the spin-only moment (2.83 Bohr magnetons) but well within the range observed for d^8 Ni atoms. On heating to 400°C, the magnetic behavior of the composite changes as shown in Fig. 4. The observed behavior is neither that of a paramagnetic substance nor that of a bulk ferromagnet. However, it does exhibit features that may be attributed to magnetically ordered particles or to ordered domains within particles. In fact, the particles are strongly drawn to a magnet as if they were ferromagnetic. The magnetization of the heated composite increased with applied field up to 15,000 G but did not reach saturation (Fig. 5) (14).

The x-ray powder pattern of a sample heated to 400°C is shown in the inset to Fig. 1. The interlayer spacing of the heated sample is 14.6 Å. The elimination of acetate ion and water molecules and the splitting out of water from the hydroxyl groups are responsible for the reduction in the interlayer spacing. In the process the Ni ions bonded to phosphate groups must move to within 3.5 Å of the central layer and bond to it through oxygen, creating three-tiered NiO-like layers sandwiched between the zirconium phosphate layers. Because the thickness of the zirconium phosphate layer is 6.3 Å, the NiO layer is then 8.3 Å thick, a reasonable value for a threetiered Ni–O layer. During heating the sample turns gray to black, but, on standing, its original green color returns. Exposure to light as in the ultraviolet-visible spectrometer restores the black color. This feature prevented us from obtaining an electronic spectrum of the heated composite.

Interestingly, the heated composites are microporous with surface areas of 60 to 130 m²/g. The pores are relatively uniform with average diameters of ~ 10 Å. The pores may arise from defects that cause the growth of the NiO layers to terminate and these layers to exist as islands with gaps between these NiO islands. The fact that the nickel hydroxide layers are bonded to the phosphate groups of the zirconium phosphate layers before heating to elevated temperatures leads us to believe that the phosphate layers act as a template to direct the growth of the metal hydroxo layers (15).

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- Detailed measurements of both the Ni and the Co composites heat-treated in the range 400° to 700°C are in progress.
- 15. We are testing this hypothesis by carrying out similar reactions with other layered compounds and examining the structures of the interposed layers.
- This study was supported by NSF grants DMR-9107715 and INT-9015164. We thank T. Hughbanks for helpful discussions on the magnetic behavior of the composites.

9 May 1994; accepted 22 September 1994

The Validity of the "Diradical" Hypothesis: Direct Femtosecond Studies of the Transition-State Structures

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Direct studies of diradicals, the molecular species hypothesized to be archetypal of chemical bond transformations in many classes of reactions, have been made using femtosecond laser techniques with mass spectrometry in a molecular beam. These studies are aimed at "freezing" the diradicals in time and in the course of the reaction. The passage of these species through the transition-state region was observed and the effect of total energy and alkyl substitution on the rates of bond closure and cleavage was examined. The results establish the nature of these intermediates and define their existence during reactions.

F or the past 60 years, the concept of diradicals as intermediates has been hypothesized to be archetypal of chemical bond transformations in many classes of thermally activated as well as photochemical reactions. Since the development of extended Hückel theory, Woodward-Hoffmann rules, and frontier-orbital descriptions of bonding (1), diradicals have become central to the understanding of reaction mechanisms as well

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as to the predictability of reaction products, rates, and stereochemistry. One of the most well-studied reactions, both theoretically and experimentally, is the ring opening of cyclobutane to yield ethylene or the reverse addition of two ethylene molecules to form cyclobutane:

+ ||

Scheme 1.

Such a reaction is a classic case study for a Woodward-Hoffmann description of concerted reactions. The reaction may pro-

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Scheme 2. Transition-state mechanism.

Scheme 3. Diradical mechanism

ceed directly through a transition state at the saddle region of an activation barrier. Alternatively, it could proceed by a twostep mechanism, beginning with the breakage of one σ -bond to produce tetramethylene as a diradical intermediate, which in turn passes through a transition state before yielding final products. These two extreme cases are illustrated in Schemes 2 and 3 with a potential-energy curve along the reaction coordinate.

The concept, therefore, besides being important to the definition of diradicals as stable species, is crucial to the fundamental nature of the reaction dynamics: a concerted one-step process versus a two-step process with an intermediate. Such intermediates are expected to exist in a potential well at internuclear configurations between reactants and products. Accordingly, they are expected to be longer lived than transition states, such that the dynamics of their nuclear motions (vibration and rotation), unlike a concerted motion (translation), determine the outcome of the reaction; that is, product channels, product-energy distributions, and stereochemistry.

Experimental and theoretical studies have long focused on the possible existence of diradicals and on the role they play in affecting the processes of cleavage, closure, and rotation. A large number of studies have been reviewed in books and articles [see, for example, (2–5)], and we mention only the general approaches used. The experimental approach is based primarily on studies of the stereochemistry of reactants and products, chemical kinetics, and the



Fig. 1. The diradical reaction on a schematic potential energy surface. Extrusion of the carbon monoxide group from the parent molecule creates the diradical (tetramethylene) intermediate with a well-defined energy. Shown are the two channels for product formation, closure to cyclobutane or fragmentation to two ethylene molecules.

effect of different precursors on the generation of diradicals. The time "clock" for rates is internal, inferred from the rotation of a single bond, and is used to account for any retention of stereochemistry from reactants to products. Berson, Bergman, Dervan, Baldwin, and others (see below) have shown the value of this approach in studies of reaction mechanisms. Theoretical approaches basically fall into two categories, those involving thermodynamical analysis of the energetics (enthalpic criterion) and those concerned with semiempirical or ab initio quantum calculations of the potential energy surface (PES) describing the motion of the nuclei in the reaction [see (6, 7)].

Hoffmann and co-workers (8), using extended Hückel theory, have provided a PES for reaction 1 and concluded the absence of the tetramethylene diradical as a stable intermediate; they suggested that the top of the potential along the reaction coordinate is "flat," favoring Scheme 2. This flatness was important to allow the nuclei to spend some time in the region, thereby explaining the lack of stereochemical retention. Such a region, termed "twixtyl," was suggested as a possible common feature of nonconcerted reactions. Benson (9), on the other hand, estimated the enthalpy of tetramethylene to lie at least 4 kcal/mol below the experimental activation energy (62.5 kcal/mol), favoring Scheme 3. This last finding was supported by ab initio calculations by Segal (10), but more recent studies by Doubleday. Bernardi et al., Borden et al., and others have found shallow minima that survive or disappear, depending on the correction for the zero-point energy (11). In contrast, for the analogous reaction of cyclopropane, Benson's calculation (9), which assumed no cooperative effects, indicated that the trimethylene 1,3-diradical is also thermodynamically stable, whereas the ab initio calculations by Salem, Borden, Davidson, Schaefer, Doubleday, and others showed no significant stability (5, 12, 13). Recent considerations (7) of the heats of formation of relevant species have addressed some of these discrepancies. An ab initio calculation must account for the large dimensionality of the PES (see below), as the intermediate has 30 vibrational degrees of freedom. Doubleday's recent theoretical work on tetramethylene (11) suggests a definite intermediate with a free energy barrier on the minimum energy reaction path.

Experimental studies of the mechanisms involving 1,3- and 1,4-diradicals are similarly numerous and cannot be fully detailed here. Since the seminal work by Rabinovitch, Schlag, and Wiberg in 1958 (14), which suggested the involvement of a diradical in the isomerization of cyclopropane, many groups have examined the

mechanistic routes of relevant systems, from different precursors for photochemical reactions or thermal processes similar to Scheme 1. To formulate the presence (or absence) of such diradicals, stereochemical and kinetics studies were advanced by several groups [see (2–5)]. For tetramethylene, measurements of the relative rates of rotation, cleavage, and closure by Dervan and co-workers (15) provided evidence for the 1,4-diradical as a common intermediate formed by different precursors. Earlier, Brauman and Stephenson (16) suggested that the method of generation of diradicals may be the key to their difference in behavior. For trimethylene (2, 3, 7, 17), the experiments suggested that the 1,3-diradical is not stable but some of its derivatives are.

The key to the above issues is the time scale for the passage of the nuclei through the transition-state region. It was suggested that an intermediate may have a lifetime on the order of a nanosecond whereas an activated complex should exist for no more than a picosecond (18). This disparity is not cardinal as it depends, of course, on the total internal energy and on the nature of the force governing the transformation. It appears, therefore, that real-time studies of these reactions should allow one to examine the nature of the transformation and to elucidate the fundamentals of the dynamics and the concept of diradicals.

We report direct studies of the femtosecond dynamics which are aimed at "freezing" the diradicals in time and in the course of the reaction. We use precursors (cyclopentanone, cyclobutanone, and their derivatives) to generate the diradicals and to monitor the formation and the decay dynamics of the reaction intermediate or intermediates. We identify the parent or the intermediate species using time-of-flight (TOF) mass spectrometry. The concept behind the experiment is illustrated in Fig. 1 with the PES, and a schematic of the apparatus is presented in Fig. 2. To avoid collisional deactivation and other perturbations, the reaction is carried out in a skimmed molecular beam.

In the molecular beam apparatus, which is equipped with the TOF mass spectrometer, an initial femtosecond pulse decarbonylates the precursor and establishes the zero of time. The second femtosecond pulse, delayed in time, probes the dynamics of a given mass species by ionization. We could either select a specific mass and study the femtosecond temporal evolution corresponding to this species, or, for a given femtosecond delay, monitor the entire mass distribution of the reaction. As with other femtochemical studies (19), the zero of time can be established in situ when the ion signal is recorded while the two pulses overlap in time. Accordingly, the femtosecond

delay of the appearance of a given intermediate fragment can be accurately determined and its decay can be followed at longer times. By changing the pump energy, we have examined the energy dependence of the dynamics. Also, we have studied polarization and power dependencies, and, for the effect of initial geometry, substitution influence on the rates.

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The experimental apparatus has been described in detail elsewhere (19). Briefly, a colliding pulse mode-locked ring dye laser generated the femtosecond pulses around 620 nm. These pulses were amplified by a Nd:YAG (neodymium:yttrium-aluminumgarnet)-pumped four-stage dye amplifier. The output pulses were temporally recompressed to 60 fs in a sequence of four high refractive-index glass prisms. The 310-nm initiation ("pump") pulse was generated by frequency doubling a part of the output in a 0.5-mm KD*P (potassium dihydrogen phosphate) crystal. For the 620-nm probe, we used the remaining part of the output. Pump tuning experiments (334 to 280 nm) were performed by selecting a part from a white-light continuum followed by further amplification and frequency doubling. The pump and probe beams were delayed in time relative to one another in a Michelson interferometer and were then recombined collinearly and focused onto the molecular beam. The output of the TOF mass spectrometer was monitored while scanning the interferometer, which was driven in steps by a computer-controlled actuator.

The mass spectra obtained at different femtosecond time delays are shown in Fig. 3. At negative times, that is, when the probe arrives before the pump pulse, there is no signal present. At time zero, the parent mass (84 amu) of the precursor cyclopentanone is observed, while the fragment mass of 56 amu is not apparent. As the time delay increases, we observe the decrease of the 84 mass signal, and, for the 56 (or 55, corresponding to the species of interest minus one hydrogen) mass, first the increase and then decrease of the signal. The 56 mass corresponds to the parent minus the mass of CO. In addition to cyclopentanone, other precursors were studied similarly, including cyclobutanone, methyl-substituted cyclopentanones (2,2,5,5-tetramethyl, 2-methyl, and 2,2-dimethyl), and 2-cyclopenten-1-one.

Figure 4 shows time-resolved transients in which the different masses of the parent and intermediate species of three systems are detected. For the 56 mass species, the buildup time is $\tau_1 = 150 \pm 30$ fs, whereas the decay time is $\tau_2 = 700 \pm 40$ fs. The precursor cyclopentanone decays with $\tau =$ 120 ± 20 fs, and the peak of the 56 mass signal is shifted from the parent signal by Δt $= 300 \pm 50$ fs. These experiments were done at a total energy E = 82 kcal/mol (see below). When the total energy was decreased by ~5 kcal/mol, slower dynamics



Fig. 2. The femtosecond molecular beam apparatus illustrating the mass selection and the overlap of the three beams. The femtosecond pump and probe pulses, delayed in time with respect to one another, are combined collinearly before being focused onto the molecular beam. The ions produced in the interaction region are detected in a time-of-flight mass spectrometer which can distinguish between different masses.

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were observed: $\tau_1 = 240 \pm 30$ fs, $\tau_2 = 840 \pm$ 50 fs ($\Delta t = 400 \pm 50$ fs), and $\tau = 120 \pm 20$ fs. On the other hand, increasing the total energy by 18 kcal/mol, faster dynamics were observed: $\tau_1 = 100 \pm 30$ fs, $\tau_2 = 340 \pm 30$ fs $(\Delta t = 150 \pm 40$ fs), and $\tau = 120 \pm 20$ fs. At the same total energy E, substitution of methyl groups at the 2 and 5 positions leads to a drastic change: $\tau_1 = 0.9 \pm 0.2$ ps and τ_2 = 1.4 \pm 0.2 ps, for the 112 mass, whereas τ = 0.5 \pm 0.1 ps for the 140 mass. For cyclobutanone, we carried out similar experiments and observed both the decay of the parent and the buildup and decay of the intermediate: At the total energy E, the dynamics is much faster with τ_1 , τ_2 , and $\tau \approx$ 100 fs.

The reaction of carbonyls is well known to proceed through a Norrish-type α -cleavage (20), which in this case leads to the C-Cbond breakage and decarbonylation. The PES involves a reaction coordinate along the C-C bonds adjacent to the CO (21). Since the 1942 work by Benson and Kistiakowsky, the gas-phase photolysis of cyclopentanone is known to yield primarily ethylene, cyclobutane, and carbon monoxide; at a wavelength similar to our excitation energy, the yield of this channel is $\sim 90\%$ (22, 23). Therefore, the reaction path is a clear decarbonvlation with the formation of tetramethylene, as discussed by Scala and Ballan (23) and others. The tetramethylene diradical forms cyclobutane (by closure) and two ethylene molecules (by fragmentation) (see Fig. 1). The time scale for this decarbonylation depends on the state excited. In our case, it is observed to be 100 to 200 fs (Fig. 4), and this clearly indicates its promptness; as will be detailed elsewhere, this is because we prepare a high-energy state (\sim 150 nm) that correlates adiabatically to products of CO and tetramethylene. This situation is different from other cases studied at low energies (first excited $n\pi^*$ state) and where the correlation is absent and the decarbonylation takes place by a slower internal conversion or intersystem crossing, as discussed by Butler and co-workers for related systems (24). The spectrum of cyclopentanone at our energies of excitation is known (25), and indeed it exhibits broad bands of Rydberg and valence states, consistent with our time scale (26). The spectra, of course, do not have signatures of any of the subsequent dynamics of the diradical intermediate.

In our experiments, we typically use two photons (320, 310, or 280 nm) from the femtosecond pump pulse to induce the α -cleavage. At time zero in Fig. 3, we note that there is no signal for the 56 mass (at these low power levels). This result indicates that there is no fragmentation in the ion channels and that we are only observing the dynamics of the neutral diradical, which is then probed by ionization (27). Such sepa-

ration of fragmentation from ionization is one powerful feature of the femtosecond time resolution, as shown previously by several groups (19, 28). From the wavelength dependence of τ and τ_1 , and the power dependence, we can conclude that the tetramethylene is formed in a nonconcerted manner (29). It is therefore possible, from the dynamics of the parent and the intermediates, to separate the two steps responsible for the formation of the diradical and to provide directly the hitherto unknown time scale for an elementary Norrish process, as will be detailed elsewhere. Here, we shall focus attention on the dynamics of the diradicals and their intrinsic lifetimes (τ_2) .

From the data in Fig. 4, the tetramethylene and methyl-substituted tetramethylene diradicals are observed to be substantially different. Moreover, in tetramethylene, as we increased the total energy from the lowest value we studied by 5 kcal/mol to the value E(30, 31) and then by an additional 18 kcal/mol, τ_2 decreased from 840 to 700 and then to 340 fs, respectively. Considering the dynamics (19) of the nuclei at the top of the barrier, it is impossible at these velocities to obtain such time scales if a wave packet is moving translationally on a flat surface. For example, over a distance of 0.5 Å, which is significantly large on a bond scale, the time in the transition-state region will be \sim 40 fs. To explain the reported (sub)picosecond times, other nuclear degrees of freedom must be involved.

The diradical in a "basin" defines a multidimensional PES with the involvement of many degrees of freedom. At the energies of interest, the total energy E available to the diradical is greater than the barrier height (E_{o}) . If we use our energy-dependent rates $(1/\tau_2)$ and invoking RRK (Ramsperger-Rice-Kassel) theory, we obtain a barrier height of $E_0 \approx 4$ kcal/mol, taking the frequency (150 cm⁻¹ or 1/220 fs) of the reaction coordinate from the PES calculation (11); note that per mode the energy is less than E_{o} and that the calculations are microcanonical, k(E), and not k(T) [further analysis will require Rice-Ramsperger-Kassel-Marcus theory (RRKM); calculations in progress]. Doubleday's calculation (11) indicates that tetramethylene is trapped on the free energy surface, and he estimates that the total rate for closure and fragmentation should correspond to 0.4 ps at 693 K and 0.3 ps at 1130 K. If we assume that Doubleday's temperature is equivalent to a microcanonical distribution, the corresponding total internal energy is then \sim 70 kcal/mol, similar in range to our E values. Moreover, he found that the lifetime is relatively insensitive to the temperature change in this range. As noted above, when we varied the internal energy by changing the energy of the initiation pulse, the change in the lifetime is not drastic, a feature reflecting the involvement of many modes in a bound state of the diradical.

Additional support for the intermediacy



Fig. 3. Mass spectra obtained for different femtosecond delay times between the pump and probe laser pulses. The parent molecule, here cyclopentanone (84 amu), appears at zero time delay and subsequently decays. In contrast, the tetramethylene diradical intermediate (56 amu) appears later, growing in and peaking at ~300 fs, and then decays very slowly ($r_2 = 700$ fs); see text. The masses at 28 and 41 amu are due to ion fragmentation and their studies will be reported elsewhere.

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of tetramethylene came from substitution effects on the observed femtosecond dynamics. Substituting the hydrogens at the active sites (where the two electrons reside) with methyl groups increases the lifetime of the diradical from the subpicosecond to the picosecond regime (see Fig. 4). The extra stability of the diradical is the result of delocalization of electron density (hyperconjugation) and possible steric repulsion (barrier) due to alkyl substitution. Studies of such effects in these systems goes back to the 1961 work by Gerberich and Walters (32) on the thermal decomposition of methyl-substituted cyclobutanes. Finally, the results have a direct impact on product-channel distributions. With methyl substitution, the internal rotation slows down with respect to fragmentation (33), thus altering the stereospecificity.

The results in Fig. 4 show that the 42 mass for the trimethylene system exhibits much faster dynamics, 120 fs. This observation indicates that trimethylene is shorter lived than tetramethylene and that a wave-packet concerted motion is appropriate to describe the reaction. It is also interesting that the parent cyclobutanone decays on a comparable time scale of 105 ± 10 fs, indicating that the decarbonylation and the diradical rearrangement all involve minimum nuclear motions in degrees of freedom other than the reaction coordinate. Further studies of this system are required in order to

Fig. 4. (A) Femtosecond transients showing the detected ion signal of a given mass as a function of the time delay between the pump and probe laser pulses. The parent cyclopentanone (84 amu) signal simply decreases with an exponential decay time of 120 \pm 20 fs. The diradical shows a biexponential behavior, building up to a maximum ($\tau_1 = 150 \pm 30$ fs) followed by a relatively slow decay ($\tau_2 = 700 \pm$ 40 fs). (B) The buildup and decay characteristics for the 42 mass obtained from the precursor cyclobutanone; τ_1 and τ_2 = 120 ± 20 fs. As noted, in this case the fit to an exponential rise and decay is not as good, consistent with a wave packet motion. (C) Substituent effect on the time scales of the dynamics, examined with the same pump and probe lasers. The

establish the intermediates involved; cyclobutanone, unlike cyclopentanone, can give the so-called C_2 channel in which there is no direct CO elimination. Because product-state distributions are known from the work of Houston and co-workers (31), we should be able to examine the dynamics of the different channels.

With different precursors and polarizations, the entrance channel of the global PES (34) and internal rotations could also be studied. Clearly further work is needed. For example, the nature of the different configurations (gauche, trans, and so forth) should be studied. Also, the initiation of the reaction from different precursors and from cyclobutane will help the mapping of the PES and identify the dynamical routes.

These studies of reaction intermediates involving diradicals provide a real-time picture of the nuclear motions and structural changes during the reaction. The observations establish the diradical, frozen on the femtosecond time scale, as a distinct molecular species. The discovery of their time scales and elementary dynamics defines the mechanistic concept crucial to the understanding of the nature of chemical-bond changes. There is a wealth of studies awaiting these and other classes of reactions, and the approach should be general for the examination of other reactive intermediates.



1,4-diradical formed from the parent molecule, 2,2,5,5-tetramethylcyclopentanone, decays relatively slowly with a decay constant: $\tau_2 = 1.4 \pm 0.2$ ps, which is very different from tetramethylene (see text).

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 Supported by a grant from the Air Force Office of
- 30. Supported by a grant from the Air Force Unice of Scientific Research and by the National Science Foundation. We are grateful to P. B. Dervan, D. A. Dougherty, M. Okumura, J. D. Roberts, and W. von. E. Doering for the helpful discussions. We

thank J. A. Berson and B. K. Carpenter for their helpful suggestions and penetrating questions, C. Doubleday Jr. for his interest in this work and for communicating unpublished results, K. Anderson for the preparation of 2,2,5,5-tetramethylcyclopentanone, and L. Bañares for his help in the preliminary work (bulb studies) in this group. Contribution no. 8970 from the Arthur Amos Noyes Laboratory of Chemical Physics.

26 August 1994; accepted 23 September 1994

Origin of Storm Footprints on the Sea Seen by Synthetic Aperture Radar

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Spaceborne synthetic aperture radar can detect storm footprints on the sea. Coastal weather radar from Cape Hatteras provides evidence that the echo-free hole at the footprint core is the result of wave damping by rain. The increased radar cross section of the sea surrounding the echo-free hole results from the divergence of the precipitation-forced downdraft impacting the sea. The footprint boundary is the gust front; its orientation is aligned with the direction of the winds aloft, which are transported down with the downdraft, and its length implies downdraft impact 1 hour earlier at a quasi-stationary impact spot. The steady, localized nature of the storm remains a mystery.

Reynolds (1) made the first attempt to explain the reports made by seafarers that rain calms the sea. He attributed this to the turbulence associated with the shedding of vortex rings by the raindrops. A rather complete history of the variety of studies aimed at explaining the wave damping mechanism is given in (2). Unfortunately, the lack of an accepted model leaves the damping mechanism in doubt. The situation is exacerbated by the absence of well-documented observations such as photographs of the sea before and after rain.

This confusion motivated several investigators (2-4) to conduct experiments in wave tanks in which wave amplitude was measured on either side of a section of artificial rain. Unfortunately, the latter are thought to be deficient in several respects (5). The confusion is compounded by the laboratory tank experiments on the backscatter from a rain-perturbed wavy water surface (6-8). In these experiments, 14and 35-GHz radars were used at incidence angles of 30° to 40°. In all three, the presence of rain increased the radar cross section (RCS) relative to that with winds alone, thus contradicting the idea of rain damping of the short resonant Bragg waves (9) of order 1 to 2 cm. The increased backscatter or RCS of the disturbed surface at vertical polarization was attributed to the rain-induced ripples or ring waves (7), and it was proposed that one may simply add the RCS due to the ring waves to that due to the winds alone (8). But these experiments are also believed to be faulty in the same senses as those on wave damping (5). Moreover, there were no observations made downstream of the small radar footprint where one would expect turbulence to be more fully developed and damping to have taken effect (5).

Therefore, laboratory experiments on the mixing of rain with near-surface water (10) were used in (5) to deduce the damping rates. Although there were no wind waves, this work used drops of sizes up to 5.5 mm impacting both fresh and salt water at terminal velocity; neither of these conditions prevailed in the earlier work. Because the drops were warm and the receiving bath was cold, a thermocline developed; the rate of increase of the depth of the thermocline is then a measure of the average eddy viscosity (5). This is proportional to the flux of kinetic energy from the rain. However, for unknown reasons the viscosity produced by 5.5-mm drops is almost twice that of drops \leq 3.6 mm in diameter. The rate of wave damping is then determined with the use of theoretical relations (11, 12). Scaling the kinetic energy flux to a rain rate of 150 mm hour $^{-1}$, one finds the eddy viscosity to be $0.30 \text{ cm}^2 \text{ s}^{-1}$. The *e*-folding decay times in a mixed layer of fresh and salt water 10 cm deep are 0.017, 1.05, and 17.9 s for short gravity waves with wavelengths of 2, 10, and 30 cm, respectively. This compares with times of 2.4, 60, and 540 s for the same sequence of wavelengths at a molecular viscosity of 0.01 cm² s⁻¹. The decay times increase at lesser rain rates but are still

smaller than that attributed to molecular viscosity. It was then postulated (5) that the longer waves would also decay because they would no longer receive energy from the shorter ones (13).

Signatures of storm-induced effects on the sea have been seen by synthetic aperture radar (SAR) on board the SEASAT satellite (14, 15). The primary feature is an echo-free hole (EFH) surrounded by a region of enhanced RCS within a well-defined boundary. The EFH was attributed to the damping of the Bragg waves (\sim 30 cm for SEASAT), thus reducing the surface RCS and causing the EFH. The boundary of the surrounding zone of increased RCS was described as a squall line (14). In a reexamination of the latter observations (5), a directional effect was observed such that the RCS was maximum on the radar-facing boundaries of the footprint and weakest on the tangential boundaries. This is the only direct evidence of the orientation of the short resonant gravity waves and thus of the winds diverging from the downdraft that accompanies the heavier rain. The combination of rain core, collocated downdraft, surface winds diverging from the downdraft impact point, and sharp wind boundary is characteristic of a convective storm. In those cases in which the near-surface divergence is particularly sharp, the phenomenon is known as a microburst (16).

Figure 1 shows the SAR image of an area off the Atlantic coast of the United States taken at 1536 UTC on 18 July 1992 at a wavelength of 5.6 cm from the European Remote Sensing Satellite 1 (ERS-1). The three largest precipitation echoes seen at a wavelength of 10 cm by Weather Surveillance Radar 57 (WSR-57) at Cape Hatteras, North Carolina (dashed curves in Fig. 1), are accompanied by strong modulations in the surface RCS. The close association of the two leaves little doubt that the precipitation or the storm-induced winds at the surface, or both, are responsible for the alterations of the surface RCS.

Note that the EFHs occur either at the southwestern edges of the precipitation echoes or within the region of maximum reflectivity and rain rate. Convective storms formed in subtropical and temperate latitudes of the Northern Hemisphere are initiated at their southernmost ends. The region of maximum storm height, rain rate, and drop sizes are found somewhat north of the southern generating point. As noted above, the maximum flux of rain kinetic energy and the greatest eddy viscosity in the near-surface water accompanies the heaviest rain, and for rain of a particular flux, the eddy viscosity is larger where the rain is composed of drops larger than 3.6 mm. These are the zones in which the surface waves would be most rapidly damped pro-

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