Reports

Mass Spectral Studies of Surface Catalysis: The Production of Free Radicals at 40°C

Abstract. *A wide variety of free radicals can be produced thermally at temperatures as low as 40°C by a new catalytic method which provides a means for studying the mechanism of many catalytic hydrogenation-dehydrogenation processes. Initial results include the first chemical evidence for the existence of the* H_3 *molecule.*

The detection of free radical intermediates in catalytic reactions by means of mass spectrometry is not new. The earliest studies were made by Eltenton (*1*), who used an electrically heated carbon grid in a reaction zone placed in front of the pinhole leak through which a sample of the products, in a stream of excess reactants, entered the ion source. A notable improvement in both detection sensitivity and sampling geometry was made by Robertson (*2*), who placed the hot catalyst surface actually inside the ion source so that it was separated from the electron beam by only the ion repeller in the form of a thin wire gauze. Melton (*3*) further simplified Robertson's design by making the catalyst also function electrically as the ion repeller and showed that it was possible to detect free radicals within several microseconds of their desorption from a hot catalyst surface, with reactant pressures varied over a tremendous range from 10^{-8} to 1 torr in the ion chamber.

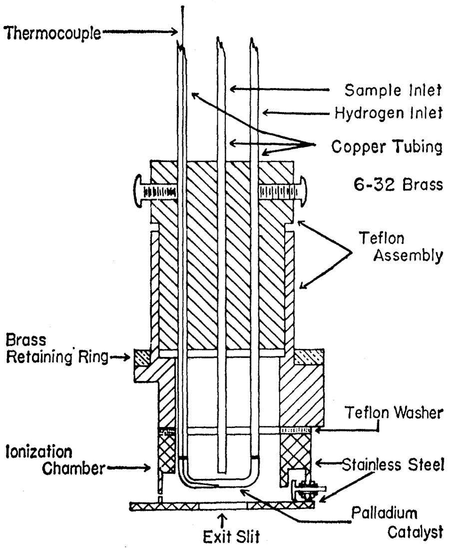

Fig. 1. Cross section of the palladium catalyst assembly.

In contrast to previous catalytic work cited here and elsewhere (*4*), whereby radicals are observed to be generated thermally only from surfaces heated above 750°C, we now report an entirely new approach for obtaining thermal radicals at temperatures as low as 40°C in such high yields that no special electron multiplication detector is required. This development has come about by focusing attention on improving the catalyst design rather than by altering the sampling geometry or by perfecting the intrinsic capability of the mass spectrometer to detect a lower concentration of radicals. We have taken advantage of two well-known properties of pure palladium metal in making an extremely active catalyst for the production of free radicals. First, palladium has an unusual affinity for abstracting and absorbing hydrogen atoms from almost any hydrogen-containing compound. The most remarkable donor substance is molecular hydrogen itself, of which palladium absorbs up to 1000 times its own volume at 25°C. Second, a thin sheet of palladium can serve as an effective semipermeable membrane through which absorbed hydrogen atoms will spontaneously diffuse away from that surface exposed to a selected hydrogen donor. In so doing, the catalyst metal functions so as to separate hydrogen atoms from hydrogen-deficient radicals left behind to accumulate on the surface. Consequently, since back reactions with hydrogen atoms are inhibited, the radicals are free to react with each other or to desorb from the catalyst surface.

The assembly designed to utilize these properties of palladium is shown in Fig. 1. The catalyst is in the form of a tube (inner diameter of 0.25 cm with a wall thickness of 0.008 cm) soldered with gold at each of its bent ends to two straight copper-connecting tubes. One of these copper tubes serves as a thermocouple well into which is inserted a Xactpak (*5*) iron-constantan thermocouple probe (outer diameter of 0.05 cm) for measuring the catalyst temperature. The other copper tube, labeled "hydrogen inlet," can be used in either of two ways: (i) as an inlet system for introducing molecular hydrogen by its diffusion from inside the catalyst out into the ionization chamber, or (ii) as a vacuum connection by which the direction of diffusion can be reversed when the catalyst is used to absorb hydrogen atoms by exposing its outer surface to a selected hydrogen donor introduced into the ion chamber through the sample inlet tube. Each of the three copper connecting tubes shown are made from an alloy (Berylco 25) to give them added hardness for resisting deformation and consequent binding when slipped through the snug-fitting holes in the Teflon assembly.

Electrically, the catalyst also acts as the ion repeller. For maximum detection efficiency it is placed parallel to and in the same plane as both the electron beam (not shown) and the

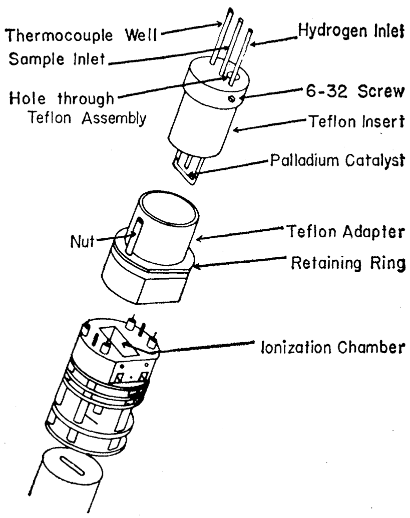

Fig. 2. The catalyst and ion source assemblies.

exit slit. Because of the heat generated by the electron filament, the catalyst has an ambient temperature of about 40°C; but it can be conveniently heated up to 450°C, without decomposing the Teflon assembly by means of a suitably isolated a-c power supply "floating" at the ion repeller voltage. A detailed description of the dimensions of the ion source, operating voltages, construction features, and general operating characteristics of the Vanderbilt higher-pressure mass spectrometer used in this study was given in an earlier report (*6*). The manner in which the new palladium catalyst assembly fits on our previous ion source assembly is shown in Fig. 2. The large hole through the Teflon assembly enables the reaction products to be removed from the ionization chamber, and also allows the pressure measured by the ion gage (not shown) outside the ion chamber to be a good estimate of the pressure at the surface of the catalyst. This arrangement also prevents the ion gage from interfering with reactions taking place in the ion chamber.

Evidence for the production of methyl radicals from our type of palladium catalyst using only a Cary Model 31 vibrating reed electrometer as the ion detector is given in Fig. 3. In this experiment the catalyst at 40°C was exposed to methane at a pressure of 5.0×10^{-4} torr. The electron beam energy was set at 10.5 ev, which is well below the ionization potential of the methane, but sufficiently high to ionize desorbed methyl radicals accounting for the more abundant mass-15 peak observed. The less prominent mass-16 and -17 peaks arise from two consecutive homogeneous ion-molecule reactions, which follow the initial ionization of the desorbed methyl radicals.

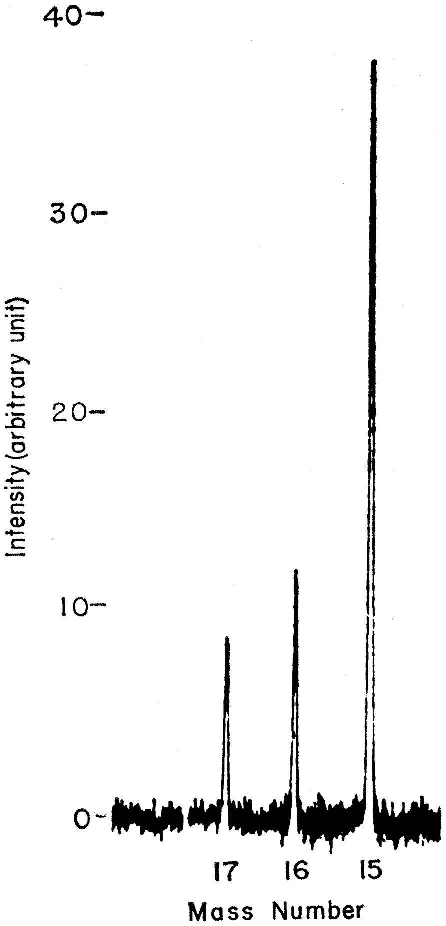

Fig. 3. Production of methyl radicals on palladium at 40°C.

$$CH_3^+ + CH_4 \rightarrow CH_4^+ + CH_3 \quad (1)$$

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3 \quad (2)$$

These ion-molecule reactions are further enhanced because each in turn produces another methyl radical precursor helping to regenerate the same chain of events. Earlier studies of the thermal generation of methyl radicals from methane (*1, 2*) were carried out at temperatures at least 700°C higher than the present work, attesting to the remarkable efficiency of this new catalyst technique. Further proof that our catalyst functions by stealing hydrogen atoms from the methane donor is the fact that hydrogen gas can be pumped off and collected from inside the catalyst tube while passing methane over its outer surface.

One of the most obvious of the possible applications of this catalyst is its use in probing the mechanism of heterogeneous hydrogenations. We are currently making a comprehensive survey of the hydrogenation of various triple bond species, such as the acetylenes and alkyl cyanides. The example shown in Fig. 4 is taken from our study of methyl cyanide at a catalyst temperature of 85°C. In this work the pressure of hydrogen gas inside the catalyst was fixed at 225 torr while methyl cyanide at 10^{-5} torr was streamed over the outside surface. The rate of diffusion of hydrogen through the wall of the catalyst was controlled by adjusting the catalyst temperature, and the electron beam energy was set at 15.5 ev to obtain a good yield of the parent positive ion, mass-41. Instead of getting a gradual distribution of the higher masses, such as 42 > 43 > 44 > 45, as would be expected if hydrogen atoms available from the catalyst were added one at a time to the cyanide substrate, we observed an unusual abundance of a mass-44 species whose relative yield with respect to the mass-41 peak of the parent cyanide increased with increasing temperature at a faster rate than any of the other peaks above the parent ion. This prominent mass-44 peak cannot be explained on the basis of a homogeneous ion-molecule reaction involving methyl cyanide, since this possibility has been excluded on the basis of an earlier study (*7*); furthermore, the pressure of 10^{-5} torr in the ion chamber is far too low to expect these processes. Nor can it be formed by the electron bombardment of possible hydrogenated products such as ethyl amine, because the mass-45 peak is far too small. Thus, we conclude that the mass-44 peak must be formed by the ionization of an intermediate radical species (C_2H_6N) desorbed from the catalyst.

The question then arises as to how

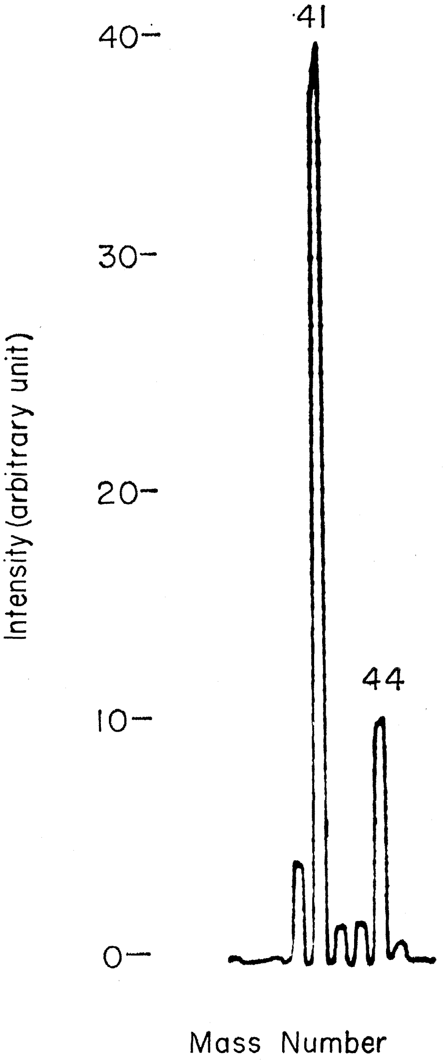

Fig. 4. The hydrogenation of methyl cyanide on palladium at 85°C.

the C_2H_6N radical becomes the most abundant of the higher mass species to desorb from the catalyst. A satisfactory explanation which is, in our opinion, supported by other data with the palladium catalyst, is that perhaps there are two kinds of "active" hydrogen atoms to be considered here. One type is simply a single hydrogen atom which is capable of an independent existence when formed in the gas phase or which dissociates into a proton and electron when diffusing through the palladium metal. But there may be another type, a more complex form of "active" hydrogen, which can be stabilized only on the surface of palladium. This form is better thought of as an H_3 molecule capable of adding in one step to the triple bond of methyl cyanide to account for the peculiar mass-44 species we observe. If this interpretation is correct, this will be the first piece of chemical evidence for the existence of the H_3 molecule. Additional support for our H_3 hypothesis is the fact that when we try to observe what species desorb when pure molecular hydrogen diffuses through our palladium catalyst, no positive mass-1 species are detectable below the ionization potential of H_2. This result indicates at least that single hydrogen atoms do not leave the catalytic surface; it may also suggest that single hydrogen atoms as such are not present on the palladium surface. However, above the ionization potential of H_2, we do obtain large yields of both masses 2 and 3. Thus far we have failed in all our attempts to distinguish between the two possible reactions,

$$H_3 + e^- \rightarrow H_3^+ + 2e^- \tag{3}$$

$$H_2^+ + H_2 \rightarrow H_3^+ + H \tag{4}$$

which could account for the mass-3 species observed under these conditions. If H_3 exists long enough to desorb and be ionized by the electron beam according to reaction 3, then our inability to prove that this reaction takes place must be because the ionization potential of H_3 is slightly greater than that of H_2.

Although much more work must be done to establish the validity of our hypothesis for the existence of the H_3 molecule, we have no doubt that the palladium catalyst technique reported here is applicable to a wide range of other surface chemical problems.

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References and Notes

1. G. C. Eltenton, *J. Chem. Phys.* **15**, 455 (1947); *J. Phys. Chem.* **52**, 463 (1948).
2. A. J. B. Robertson, *Proc. Roy. Soc. London, Ser. A* **199**, 394 (1949).
3. C. E. Melton, *J. Chem. Phys.* **35**, 1751 (1961); *ibid.* **33**, 647 (1960).
4. A. G. Harrison, in *Mass Spectrometry of Organic Ions*, F. W. McLafferty, Ed. (Academic Press, New York, 1963), pp. 221–224.
5. Claud S. Gordon Co.
6. T. W. Martin, R. E. Rummel, C. E. Melton, *Science*, **138**, 77 (1962).
7. T. W. Martin and C. E. Melton, *J. Chem. Phys.* **32**, 700 (1960).
8. We gratefully acknowledge the support of this work under U.S. Atomic Energy Commission contract AT-(40-1)-2825.

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Precaution in the Use of Iodine-125 as a Radioactive Tracer

Abstract. *The absorption of the low-energy radiation from iodine-125 under certain circumstances may be a serious disadvantage in its use as a radioisotopic tracer.*

The advantages of iodine-125 over iodine-131 as a radioactive tracer isotope of iodine have been reviewed recently by Daniel *et al.* (*1*). A limitation in the use of I^{125} has been observed, however, in that a high proportion of the gamma radiation derived from this isotope is absorbed by solutions of certain electrolytes, for example, cesium chloride and potassium iodide. Although this absorptive effect could have been predicted from theoretical considerations, and is obvious to the physical scientist, other biologists may overlook this point, as we did, in changing from the use of I^{131} to I^{125}.

During a study of the possible incorporation of 5-iodo-2′-deoxyuridine-I^{125} into viral DNA (*2*), it was observed that an aqueous solution of radioactive DNA, labeled with 5-iododeoxyuridylic acid-I^{125}, appeared to "lose" as much as 80 percent of its radioactivity, as measured by a gamma-scintillation counter, when recovered from a cesium-chloride density gradient. Investigations were therefore made on the effect of solutions of cesium chloride, rubidium chloride, potassium hydroxide, and potassium iodide on the efficiency of counting the gamma radiation from either I^{125} or I^{131} (Fig. 1). The effect of substances of various densities on the transmission of gamma radiation was determined by means of a pair of concentric tubes, with the isotope in the inner tube and the absorbing material in the outer annular space (Table 1).

Samples of constant volume were counted in a well-type scintillation detector, with a NaI (Tl) crystal and a pulse-height analyser and scaler; in order to maintain a low statistical error, at least 3000 counts were registered.

The results show that, in all conditions studied, the absorption by the electrolyte or solvent of the gamma radiation from I^{125} ($E = 0.035$ Mev) was much greater than that from I^{131} ($E = 0.36$ Mev) and is affected more by the atomic numbers of the constituents of the absorber than by its density. The absorption of gamma radiation by matter is a summation of several specific absorption modes, and for radiation of low energy, that is, <0.1 Mev, the predominant mode is dependent on the fifth power of the atomic number of the absorber. Thus the variation of absorption with atomic number is not linear but soon approaches a limiting asymptotic value. This is seen here with the chlorides of rubidium (atomic number 37) and cesium (atomic number 55), where an increase of 18 in the atomic number has no effect on the magnitude of the absorption, but a decrease of 18, that is, potassium (atomic number 19), practically abolishes the absorption. The higher energy radiation from I^{131}, however, is almost totally unaffected by the same absorbers. The radioactivity "lost" by I^{125}-labeled DNA in such an absorbing solution may be "recovered" by separation of the DNA-polymer from the absorbing electrolytes by any one of a number of procedures, such as dialy-

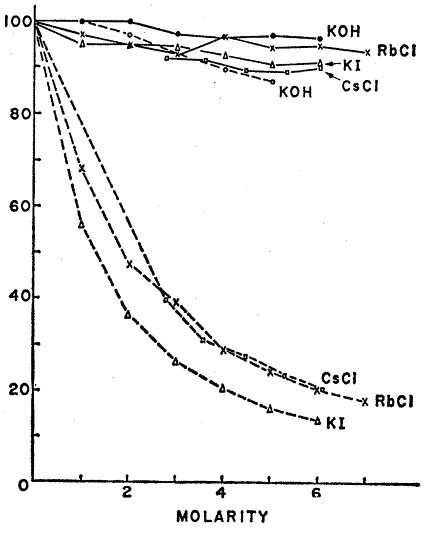

Fig. 1. The effect of various compounds on the transmission (percent) of gamma radiation derived from I^{131} (solid lines) and I^{125} (dotted lines).