foil sample is 5 × 10^{-3} μm^3, the smallest single crystal volume studied by x-ray diffraction methods. This volume is a factor of 6 smaller than that investigated by Skelton *et al.* (*19*) (3 × 10^{-2} μm^3) and one-fourth that studied by Ohsumi *et al.* (*20*) (2 × 10^{-2} μm^3). In the latter two cases, the diffracting volume was determined by the volume of a tiny sample completely bathed by a much larger beam. However, for the study of small crystal volumes, our microbeam technique improves the signal-to-background ratio, allowing the study of even smaller crystal volumes in the future.

At the present time, tapered capillaries are the only x-ray optical component producing nanometer spatial resolution with high-energy x-rays. We anticipate that many new experiments will be possible with these ultrasmall diameter x-ray beams.

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Free-Radical Side-Chain Bromination of Alkylaromatics in Supercritical Carbon Dioxide

James M. Tanko* and Joseph F. Blackert

Free-radical side-chain brominations of alkylaromatics in supercritical carbon dioxide (SC-CO_2) are reported. Direct bromination of toluene and ethylbenzene form the corresponding benzyl bromides in high yield. The observed selectivity in SC-CO_2 is similar to that observed in conventional organic solvents. Also, SC-CO_2 is an effective alternative to carbon tetrachloride for use in the classical Ziegler bromination with *N*-bromosuccinimide. Reaction yields are high, side products are minimized, and bromine-atom selectivities are observed. Thus, SC-CO_2 must be useful as a viable, environmentally benign substitute for many of the solvents typically used for free-radical reactions.

The need to reduce or eliminate toxic chemical wastes and by-products in chemical manufacturing requires the development of new synthetic methods that use compounds that are less toxic and more environmentally benign (*1*). For certain reactions, the solvents that have been selected for their chemical inertness are highly halogenated compounds that are not environmentally benign [such as chlorofluorocarbons (CFCs) and carbon tetrachloride (CCl_4)].

One such class of reactions are free-radical brominations of alkylaromatic compounds such as toluene. Reaction of molecular bromine with an alkylaromatic in a suitable solvent, initiated either photochemically or thermally with a free-radical initiator, produces the corresponding benzylic bromide in nearly quantitative yield. The mechanism of the reaction (Fig. 1) involves a free-radical chain process in which (i) hydrogen abstraction by atomic bromine ($Br^{\cdot}$) generates a benzyl radical ($PhCH_2^{\cdot}$) and HBr and (ii) trapping of $PhCH_2^{\cdot}$ by molecular bromine produces benzyl bromide and regenerates $Br^{\cdot}$. Long chain lengths are observed for these reactions, and the selectivity associated with hydrogen abstractions by $Br^{\cdot}$ is very high (generally the weakest C–H bond in the substrate is broken) (*2*).

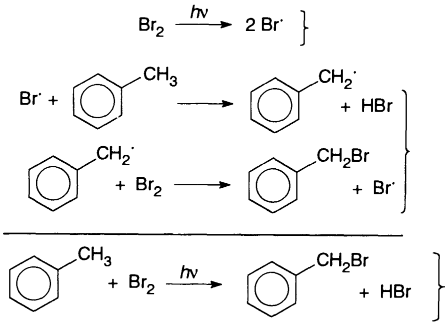

Fig. 1. Free-radical bromination of toluene. Initiated photochemically (top bracket; *h* is Planck's constant, *ν* is the frequency of the radiation), bromination propagates by the next two reactions (middle bracket). The overall reaction (bottom bracket) is shown below the summation line.

Suitable solvents for this reaction (such as CFCs and CCl_4) must not have abstractable hydrogen atoms or reactive double bonds. An appropriate replacement solvent would be SC-CO_2 because of its virtual nontoxicity and its solvating properties (*3*). There are important issues that must be addressed in the assessment of the utility of SC-CO_2 as a solvent for radical reactions: Is SC-CO_2 inert toward free radicals? Are reaction yields compromised by the use of SC-CO_2? How are reactivity and selectivity affected in SC-CO_2 medium?

There have been few reports that address these issues. Leffler and co-workers reported that the decomposition of diacyl peroxides in SC-CO_2 yields products derived from both radicals and ion pairs (*4*). McHugh and co-workers reported the first example of a free-radical chain reaction in SC-CO_2, the oxidation of cumene (*5*). Fox, Johnston, and co-workers studied the dimerization of the benzyl radical (generated by photolysis of dibenzyl ketone in SC-CO_2) and noted a distinct absence of cage effects (*6*). Chateauneuf and co-workers reported absolute rate constants for hydrogen-atom abstraction by triplet benzophenone from several donors and noted an intriguing effect of pressure (*7*). DeSimone and co-workers examined the kinetics of decomposition of the free-radical initiator 2,2′-azobis(isobutyronitrile) (AIBN) in SC-CO_2 and also reported the free-radical polymerization of 1,1-dihydroperfluorooctyl acrylate (FOA) (*8*).

We studied the reaction of Br_2 with toluene and ethylbenzene in SC-CO_2 (*9*) (Table 1). The major products of these reactions are the corresponding benzylic

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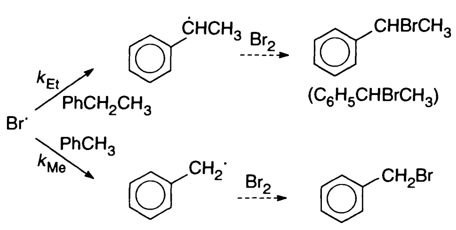
Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061–0212

*To whom correspondence should be addressed bromides formed in high yield. In the case of toluene, a small amount of *p*-bromotoluene is also formed, arising from a competing electrophilic processes.

Evidence that Br˙ was the chain carrier in these reactions (as opposed to a Br˙-CO$_2$ complex or adduct) (*10*) was provided by the competitive bromination of ethylbenzene and toluene (Scheme 1; k_{Et} and k_{Me} are rate constants; Et, ethyl; Me, methyl).



Scheme 1

If the initial concentration of Br$_2$ is much less than that of PhCH$_3$ and PhCH$_2$CH$_3$, the reactivity of the "secondary" (2°) hydrogens of ethylbenzene relative to the "primary" (1°) hydrogens of toluene on a per-hydrogen basis, $r(2°/1°)$, can readily be calculated from product yields

$$r(2°/1°) = \frac{k_{Et}}{k_{Me}}\,\frac{3}{2}$$

$$= \frac{\text{yield } C_6H_5CHBrCH_3}{\text{yield } C_6H_5CH_3}\;\frac{[PhCH_3]_i}{[PhCH_2CH_3]_i}\;\frac{3}{2}$$

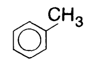
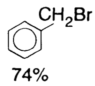
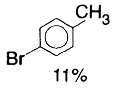
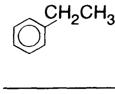
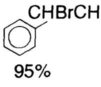
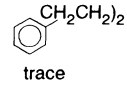
where brackets denote initial concentration of species. The results are summarized in Table 2.

Table 2. Relative reactivity of the benzylic hydrogens of ethylbenzene and toluene toward bromine atom in SC-CO$_2$ at 40°C.

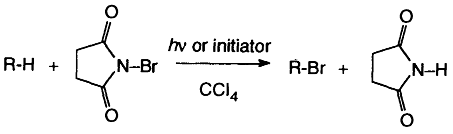
Pressure (bar)	r(2°/1°)
75	30 ± 2
79	31 ± 2
111	28 ± 2
119	30 ± 2
247	25 ± 2
339	32 ± 2
423	30 ± 2

The observed selectivities in SC-CO$_2$ are nearly identical to that observed in conventional organic solvent: $r(2°/1°)$ = 25 in CCl$_4$ at 77°C (*11*) and $r(2°/1°)$ = 36 in CCl$_4$ at 40°C (*12*). The fact that the selectivity is the same in SC-CO$_2$ and CCl$_4$ strongly implicates free Br˙ as the chain carrier in SC-CO$_2$. Selectivity, within experimental error, is nearly invariant with pressure. The expected variation of a rate constant k with pressure P derived from transition state theory is $(\delta\ln(k)/\delta P)_T = -\Delta V_{act}/RT$, where R is the gas constant, T is temperature, and the volume of activation (ΔV_{act}) is the difference in molar volume between the transition state and reactants (*13*). The invariance of $r(2°/1°)$ with pressure can be explained because the difference in the volume of activation for hydrogen abstraction from ethylbenzene versus toluene by Br˙ is small ($\Delta\Delta V_{act}$ = −4.8 cm^3/mol) (*14*). On this basis, over the range of pressures examined in this work (~75 to 400 bar), the relative reactivity would vary by <10% (that is, the anticipated pressure effect is of the same magnitude as experimental error).

Table 1. Products and yields of the free-radical bromination of alkylaromatics in SC-CO$_2$ at 40°C. Conditions: (top) 2.0 mmol toluene, 0.98 mmol Br$_2$, and 252 bar CO$_2$; and (bottom) 2.0 mmol ethylbenzene, 0.20 mmol Br$_2$, and 229 bar CO$_2$.

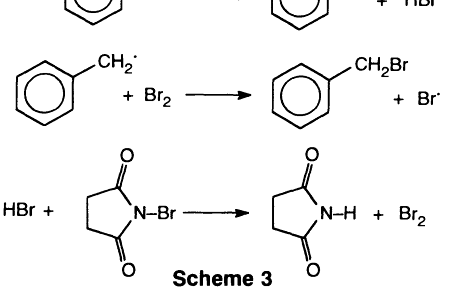
Reactants	Products	
	 74%	 11%
	 95%	 trace

The Ziegler bromination is an important method for the synthesis of allylic and benzylic bromides (Scheme 2; R is allylic or benzylic; SH is succinimide) (*15*). Critical features of this reaction include the use of *N*-bromosuccinimide (NBS) as the brominating agent and CCl$_4$ as reaction solvent. The advantage of the Ziegler method over direct bromination with Br$_2$ is that competing electrophilic processes are virtually eliminated.



NBS **Scheme 2** SH

The mechanism of the Ziegler bromination involves a bromine atom as the hydrogen abstractor (Scheme 3). NBS serves only to produce Br$_2$ in a low, steady-state concentration from the HBr by-product formed during the course of the reaction. The CCl$_4$ solvent is critical to the success of this reaction because NBS is insoluble in CCl$_4$ (the use of solvents in which NBS is soluble leads to an alternative pathway involving the intermediacy of succinimidyl radical) (*16*).



Scheme 3

The classical Ziegler bromination can be conducted in SC-CO$_2$. Irradiation of a solution containing 3.8 mmol toluene, 1.2 mmol NBS, and 0.12 mmol AIBN (initiator) in SC-CO$_2$ (170 bar, 40°C) for 4 hours yielded benzyl bromide in quantitative yield with no detectable amount of *p*-bromotoluene. The reaction was heterogeneous as NBS was observed to be insoluble in SC-CO$_2$. The competitive Ziegler bromination of ethylbenzene and toluene in SC-CO$_2$ (40°C, 342 bar) yielded a relative reactivity $r(2°/1°)$ = 29 ± 2, identical to that observed with direct bromination with molecular bromine (Table 2). This result implicates Br˙ as the chain carrier for the Ziegler bromination in SC-CO$_2$ and suggests that there is no change in mechanism with the conversion from CCl$_4$ to SC-CO$_2$ solvent.

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9. For the SC-CO$_2$ reactions, a sealed glass ampule containing Br$_2$ (degassed) was introduced into a high-pressure reactor (~25-ml capacity) equipped with a sapphire window for irradiation and a magnetic stir bar. The alkylaromatic, previously degassed by bubbling argon, was introduced into the reactor through a syringe under argon backflush. The reactor was sealed, pressurized with CO$_2$ to the desired pressure (during which time the Br$_2$ ampule usually ruptured), and equilibrated at 40°C for 5 to 10 min. The critical temperature and pressure for CO$_2$ are 31°C and 74 bar, respectively [R. C. Weast, Ed., *Handbook of Chemistry and Physics* (CRC Press, Cleveland, OH, ed. 55, 1974)]. The Br$_2$ color was evident in solution until exposure to ultraviolet light (supplied by a 400-W medium-pressure mercury arc lamp). Once irradiated, Br$_2$ color dissipated in less than 5 min. After reaction, we depressurized the cell by bubbling the contents through hexane. After the reactor had returned to ambient pressure, the cell was washed repeatedly with hexane. The combined hexane washings were analyzed by gas chromatography versus an appropriate internal standard.
10. Chlorine atom selectivities vary when free-radical chlorinations are conducted in CS$_2$ solvent because of formation of a Cl˙-CS$_2$ complex See G. A. Russell, *J. Am. Chem Soc.* **80**, 4897 (1958); J. E. Chateauneuf, *ibid.* **115**, 1915 (1993)

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13. If the rate constant k is not expressed in concentration-independent units such as mole fraction or molality, an additional factor must be included to account for the compressibility of the solvent. For rate constants expressed in units of molarity, the full expression is $[\delta \ln(k)/\delta P]_T = -\Delta V_{act}/RT + \Delta m[\delta \ln(\rho)/\delta P]_T$, where Δm is the difference in the stoichiometric coefficients of the products and reactants and ρ is the solution density. See C. D. Ritchie, *Physical Organic Chemistry, The Fundamental Concepts* (Dekker, New York, ed. 2, 1990), pp. 74–75.
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Quantum Yield for Production of CH_3NC in the Photolysis of CH_3NCS

Ramón A. Alvarez and C. Bradley Moore*

The ultraviolet spectrum of methyl isothiocyanate (CH_3NCS) and the quantum yield for its dissociation into methyl isocyanide (CH_3NC) and atomic sulfur at 308 nanometers, $\Phi = 0.98 \pm 0.24$, were measured. Methyl isothiocyanate is widely used as an agricultural fumigant and readily enters the atmosphere during and after application. The results indicate that photodissociation by sunlight is an effective pathway for its removal from the atmosphere.

Methyl isothiocyanate (CH_3NCS, MITC) is widely used in agriculture as a soil fumigant; it is a toxic substance that irritates the skin and mucous membranes (*1*). In 1991, 2.1×10^4 metric tons of metam-sodium, which decomposes in the soil to yield MITC,

$$CH_3NHCS_2{}^-Na^+ \rightarrow CH_3NCS + NaHS$$

were used in the United States (*2*). The California Policy Seminar lists metam-sodium fourth in its priority ranking of high profile pesticides on the basis of 1990 data on applied volumes (*3*). Because of its high vapor pressure (~13 torr at 297 K), MITC can enter the troposphere by spray drift during application or by subsequent volatilization. Estimating that ~60% of the applied dosage of metam-sodium is emitted as MITC into the air (*4*), one finds that $\sim 10^4$ metric tons of MITC were released into the atmosphere in 1991. Concentrations as high as 3 to 242 $\mu g\ m^{-3}$ [1 to 81 parts per billion (ppb)] have been measured at sites downwind from fields injected with metam-sodium (*5, 6*). The threshold for toxicity of MITC is presently under debate; levels above 1 ppb may cause discomfort in some members of the population (*7*).

The persistence of pollutants in the atmosphere may pose health and environmental risks. To assess the potential risks arising from the use of toxic substances, we need to know the dominant mechanism and the rate for their removal from the atmosphere. The fate of species in the troposphere is determined by some combination of (i) photodissociation; (ii) chemical removal, for example, reaction with other trace species such as OH and O_3; and (iii) physical removal, such as through dry deposition or rainout (*8*). This report, which deals with the fundamental photochemistry of MITC, indicates that solar photodissociation could be the chief removal pathway of MITC.

Published ultraviolet (UV) (*9*) absorption spectra of MITC do not cover the spectrum at wavelengths of significant solar flux (wavelengths $\lambda \geq 295$ nm). The NCS radical in various electronic states has been detected as a product of the UV and vacuum-UV photolysis of MITC by a wavelength-selected broadband source (*10*), synchrotron radiation (*11*), and excimer lasers (*12*), as well as from electron impact on MITC (*13*). The photolysis of MITC at 248 and 193 nm also produces small amounts of CN (*12*). The decomposition of MITC in a discharge has been observed to yield NCS (*14, 15*) and CS, CN, and S_2 (*15*). The production of $S(^3P)$ atoms and CH_3NC in solutions of MITC irradiated with 254-nm light has also been reported, with a maximum yield of 45% (*16*). However, nothing is known about the photolysis of MITC at energies corresponding to the long-wavelength tail of its lowest energy absorption band, and the quantum yields of the photolysis products have not been quantified at any wavelength.

The absorption cross section, σ, of MITC is shown in Fig. 1. We focused on the long-wavelength tail that overlaps the spectrum of solar, or actinic, flux (*17*). The absorption band extends out to at least 340 nm, but the wavelength interval from 305 to 330 nm accounts for 86% of the total rate for MITC absorption of the actinic flux in the troposphere. For a photodissociation quantum yield of 1.0, a total absorption rate of $6.7 \times 10^{-6}\ s^{-1}$ yields a lifetime with respect to photolysis of 41 hours for noon sunlight on 1 July at a latitude of 40°N (Table 1). The MITC absorbance was linear in MITC pressure from 1.0 to 9.7 torr. The relative uncertainties in the cross sections at the 95% confidence level were 3, 8, and 23% at 300, 320, and 330 nm, respectively. With a conservative estimate of ±10% for the systematic error in the cross-section determination, the reported values and polynomial fit to the spectrum in Table 1 are believed to be correct to within 10% for $\lambda < 300$ nm, 15 to 20% for $300 \leq \lambda < 320$ nm, and 30% for $320 \leq \lambda \leq 330$ nm. Despite the magnitude of these uncertainties, it is clear that photochemical degradation in the atmosphere could be an effective removal pathway if the photodissociation quantum yield were sufficiently high. We explored this possibility by quantitatively

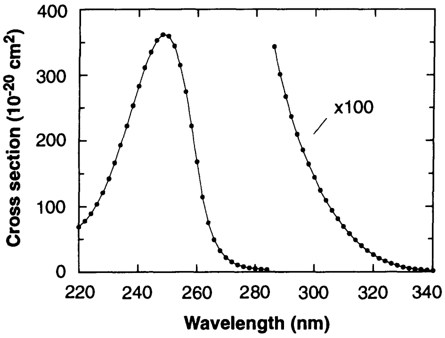

Fig. 1. Ultraviolet spectrum of CH_3NCS. The spectrum was acquired on a Hewlett-Packard 8452 UV/VIS spectrometer with a resolution of 2 nm. The CH_3NCS was pumped at 195 K before use to remove any CS_2 impurity, as verified by mass spectrometry and FTIR spectroscopy (CS_2 concentration $\leq$ 0.5%). An 8.0-cm quartz cell held the sample, and the evacuated cell served as the blank for all scans. We determined the 100% transmittance level by averaging the percent transmittance values in the 340- to 360-nm range where no signal was detected. All spectra were taken at 298 ± 2 K where $\sigma = A/[P(\text{MITC}) \times (3.25 \times 10^{16}) \times 8.0]$; A is the absorbance (base e), and P is the pressure (in torr).

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