

by aqueous soluble photoinitiator  $\beta$ -ketoglutaric acid (KGA) nor the aqueous thermal initiator sodium persulfate (SP) varied with application of an external magnetic field. Thus, the effect is unique to oil-soluble photoinitiators.

What is the mechanistic basis of the magnetic field effect and at what stage(s) of the polymerization does it operate? From our recent work<sup>5</sup> on cage reactions of triplet radical pairs in micelles, we postulate that it is the Zeeman splitting of the  $T_{\pm}$  triplet levels from the singlet level which causes the magnetic field effect by decreasing  $T_{\pm} \rightarrow S$  intersystem crossing and thereby allows for an increase in the efficiency of radical escape. A more efficient escape of radicals simultaneously allows a more efficient initiation of polymerization and formation of a greater number of polymer particles (by reducing the extent of radical pair combination in micelles), a more efficient overall initiation (by escaping radicals which enter other micelles), and a less efficient termination (by inhibiting the extent of combination of propagating radicals and initiator radicals). This postulate is consistent with the relatively low magnetic fields needed to influence polymerization. Furthermore, the efficiency of  $C_6H_5^{13}CH_2CO^{13}CH_2C_6H_5$  (DBK- $^{13}C$ )<sup>9</sup> as a photoinitiator is significantly less than that of DBK. For example,<sup>10</sup> under comparable conditions DBK as initiator produces a 52% yield of polymer ( $M_r = 4.0 \times 10^6$ ) in 5 h, whereas DBK- $^{13}C$  as initiator produces a 13% yield of polymer ( $M_r = 1.4 \times 10^6$ ) for the same time period. We interpret this to mean that recombination of  $C_6H_5^{13}CH_2 \cdot ^{13}CH_2C_6H_5$  radical pairs in micelles is more efficient than that of  $C_6H_5^{12}CH_2 \cdot ^{12}CH_2C_6H_5$  radical pairs. Finally, the efficiency of EP with 4,4'-di-*tert*-butyldibenzyl ketone (DTB) is drastically reduced relative to DBK. For example,<sup>11</sup> under comparable conditions, DBK as initiator produces a 68% yield of polymer ( $M_r = 3.9 \times 10^6$ ) in 27 h, whereas DTB as initiator produces a 16% yield of polymer ( $M_r = 1.0 \times 10^6$ ) for the same time period. We interpret this to mean that the more hydrophobic 4-*tert*-butylbenzyl radicals cannot escape from micelles as efficiently as benzyl radicals. The further findings that there are no magnetic field effects on the EP of styrene with water-soluble initiators (SP and KGA) or with oil-soluble initiators that thermolyze to produce micellized singlet radical pairs [azobis(isobutyronitrile) and dibenzoyl peroxide] lend support to the conclusion that micellized triplet radical pairs are required for the observation of magnetic field effects.

Experiments were run in order to establish which stage of polymerization was most sensitive to magnetic field effects. Experiments were conducted under three sets of conditions: (1) photoinitiated EP was run to ~20% conversion in the earth's field for ~1.5 h and then for a comparable period of time at 1000 G; (2) photoinitiated EP was run to ~20% conversion at 1000 G for ~40 min and then for a comparable period of time in the earth's field; (3) photoinitiated EP was run to 20% conversion in either the earth's field or at 1000 G and then the system was allowed to stand in the dark for ~1 h. It was found that the initial stage determined completely the  $M_r$  characteristics of the product and that no reaction occurs after the first stage in the dark.

In summary, EP of styrene, photoinduced by an oil-soluble initiator, can proceed to high conversions at convenient rates and produce a polymer of  $M_r$  comparable to that achievable in conventional EP by employing a water-soluble initiator. Weak magnetic fields have a significant effect on the EP of styrene only

when oil-soluble initiators are employed.<sup>12</sup> The magnetic field effects appear to operate during the early (micellar) stage of polymerization and to originate from Zeeman inhibition of triplet radical coupling within micelles, which leads to the formation of a larger amount of growing polymer particles and hence to a higher  $M_r$  and polymerization rate.

**Acknowledgment.** We thank the Air Force Office of Scientific Research and the National Science Foundation for their generous support of this work.

(12) Reports of magnetic field effects on solid-state radiation-induced polymerizations have been reported by Mori et al. (Mori, K.; Tabata, Y.; Oshima, K. *Kogyo Kagaku Zasshi* 1970, 73, 1215; *Ibid.* 1970, 73, 815).

Nicholas J. Turro,\* Ming-Fea Chow, Chao-Jen Chung  
Chen-Ho Tung

Department of Chemistry, Columbia University  
New York, New York 10027

Received May 5, 1980

## Activation of Methane with Photoexcited Metal Atoms

Sir:

The activation of inert bonds with transition metals has been recognized as an important goal.<sup>1</sup> Recent reports describing the oxidative insertion of diiron into a carbon-hydrogen bond of methane<sup>2</sup> and of zirconium atoms into the carbon-carbon or carbon-hydrogen bonds of isoalkanes<sup>3</sup> prompt us to report some of our results on the reactions of photoexcited metal atoms with methane.

Spectrum A (Figure 1) indicates that no reaction occurs between iron atoms<sup>4</sup> and methane at 15 K.<sup>5</sup> Irradiation with  $\lambda < 360$  nm causes a new set of peaks at 1653.4, 1153.4, 548.8, 545.9, and 521.1  $cm^{-1}$  to appear as shown in spectrum B. The isotopic shifts observed in spectra C and D indicate that the 521.1- and 1653.1  $cm^{-1}$  peaks can be assigned to the iron-carbon and iron-hydrogen stretching modes, respectively, and suggest that oxidative cleavage of a carbon-hydrogen bond has occurred to yield  $CH_3FeH$  (1). The other peaks can be assigned to the hydrogen modes of the methyl group.<sup>6</sup>

Wavelength-dependent photolysis studies indicate that reaction is caused by absorption of the metal atom rather than the metal dimer. Thus, the iron-methane matrix was first irradiated with light which could only photoexcite the assigned<sup>7</sup> electronic transition of the metal dimer; however, the photoinduced reaction was observed when light was present in the region where the free metal atom is known to absorb.

Similar results were obtained when other metals were codeposited with methane and irradiated. Thus, Mn, Co, Cu, Zn, Ag, and Au all reacted with methane to give insertion products analogous to 1, whereas Ca, Ti, Cr, and Ni failed to yield insertion products. The infrared absorption frequencies of these products are presented in Table I.

(1) J. P. Collman et al., N.T.I.S. Bulletin PB-240 177, "Workshop on Fundamental Research in Homogeneous Catalysis as Related to U.S. Energy Problems," held at Stanford University, Stanford, CA, Dec 4-6, 1974.

(2) P. H. Barrett, M. Pasternak, and R. G. Pearson, *J. Am. Chem. Soc.*, **101**, 222 (1979).

(3) R. J. Remick, T. A. Asunta, and P. S. Skell, *J. Am. Chem. Soc.*, **101**, 1320 (1979); see also S. C. Davis and K. J. Klabunde, *ibid.* **100**, 5973 (1978).

(4) Iron atom concentrations from 0.1% to 1% were used.

(5) The apparatus has been described previously: NBS Spec. Publ. (U.S.) 561, Proceedings of the 10th Materials Research Symposium on Characterization of High Temperature Vapors and Gases held at NBS, Gaithersburg, MD, Sept 18-22, 1978. Concentrations were measured with a quartz crystal oscillator mounted on the 15 K copper block.

(6) The peaks reported by Barrett, Pasternak, and Pearson<sup>2</sup> were not observed.

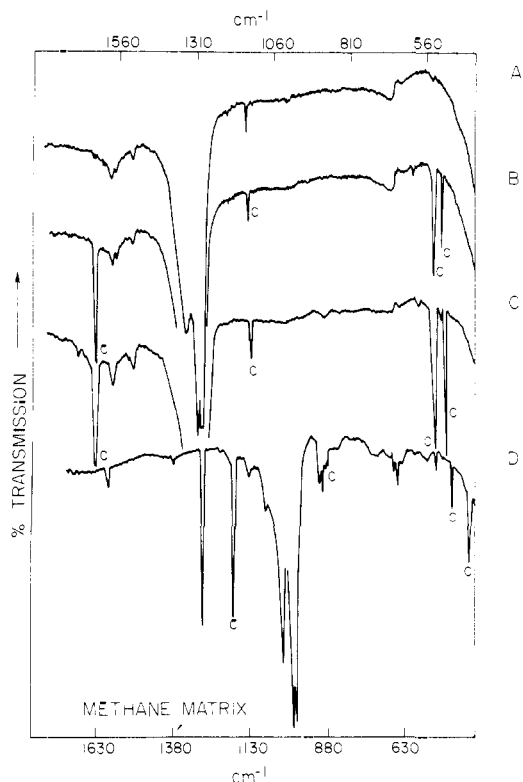
(7) T. C. DeVore, A. Ewing, H. F. Franzen, and V. Calder, *Chem. Phys. Lett.*, **35**, 78 (1975).

(8) The oxygen was removed by bubbling argon through the solution for at least 30 min at room temperature. Nevertheless, residual oxygen appears to cause the polymerization to have induction periods which vary somewhat from sample to sample. As a result, the yield of polymer was not reproducible to better than a 20% error for short polymerization periods ( $\leq 3$  h). Generally, for the magnetic field studies, the polymerization was carried out for longer than 12 h. At this stage, the conversion of polymerization is about 90%. It was found that the molecular weight is independent on the conversion range 20%-90%. The available data for the conversion of polymerizations are about 30% and 90% at 0 and 250 G, respectively, for 3-h irradiation.

(9) DBK- $^{13}C$  contains 90%  $^{13}C$  at both the 2 and 2' carbon atoms.

(10) Initial reaction concentrations: SDS = 0.05, DBK = 0.0013, DBK- $^{13}C$  = 0.0015 M.

(11) Initial reaction concentrations: SDS = 0.05, DBK = 0.0005, DTB = 0.0008 M. The low solubility of DTB requires lower initiator concentrations and forces longer reaction times.



**Figure 1.** Infrared spectra of the reaction products of iron atoms with methane. Spectrum A was recorded after trapping iron atoms vaporized at 1450 °C into a methane matrix. Spectrum B was recorded after photolysis with  $\lambda > 330$  nm. Spectrum C was recorded after trapping iron atoms vaporized at 1410 °C into a 95% [ $^{13}\text{C}$ ]methane matrix with irradiation during trapping. Spectrum D was recorded after trapping iron atoms vaporized at 1410 °C into a 95% deuteriomethane matrix with irradiation during trapping. Absorptions labeled C are product bands.

**Table I.** Product Band Positions ( $\text{cm}^{-1}$ ) in Photoexcited Metal Atom/Methane Reactions

metal atom	band positions, $\text{cm}^{-1}$			
	$\nu_{\text{C-H}}$	$\nu_{\text{M-H}}$	$\nu_{\text{CH}_3}$	$\nu_{\text{M-C}}$
manganese	2932.9	1582.6	1142.3	550.3
			546.2	
iron	2933.5	1653.1	1153.4	548.8
	2908.6		545.9	521.1
			576.7	
cobalt		1699.5	585.4	527.5
copper		1855.7	1200.1	613.8
			433.9	417.4
zinc		1845.8	1069.5	689.1
silver	2907.6	1725.8	1232.4	614.7
	2900.1			
gold		2195.8	1202.8	610.9

It is interesting that the first half of the first-row transition-metal series is unreactive with respect to photoinsertion while the second half, with the exception of nickel, is reactive.<sup>8</sup> Similar behavior was observed during recent studies<sup>9</sup> of metal atom reactions with water where all of the second half of the first-row transition-metal series (except nickel) formed a metal atom-water adduct which yielded the insertion product HOMH after photolysis. We suspect that ground-state adducts also exhibit a dominant role in the reactions under investigation here, suggesting that the nickel atom-methane adduct fails to form and that photoexcitation of the metal is then unproductive.

(8) The failure of nickel atoms to react is surprising in view of the results of Davis and Klabunde<sup>3</sup> who have shown that clusters of nickel atoms cleave carbon-carbon bonds.

(9) Unpublished observation of R. H. Hauge, A. Kauffman, and J. L. Margrave.

Prolonged irradiation at wavelengths between 200 and 300 nm causes a reduction of the peaks assigned to the  $\text{CH}_3\text{MH}$  species for Fe, Co, and Cu and leads to a new set of peaks. The loss of the metal-hydride stretch and the similarity of the low-frequency peaks suggest these metals undergo further insertion to form the  $(\text{CH}_3)_2\text{M}$  species.

The synthesis of 1 and related compounds on a macroscale level will be reported later.

**Acknowledgment.** We gratefully acknowledge the Robert A. Welch Foundation (Grants C-490 and C-109) and the National Science Foundation for support of this work.

W. E. Billups,\* Mark M. Konarski, Robert H. Hauge  
John L. Margrave

Department of Chemistry  
Rice University, Houston, Texas 77001  
Received June 30, 1980

### A Simple Highly Efficient Asymmetric Synthesis. Preparation and Absolute Configuration of 3(S)-(tert-Butoxycarbonylamino)-1(S)-methyltetra- hydrothiophenium Tosylate

Sir:

Pyramidal organosulfonium ions occur in living cells.<sup>1</sup> Some methyl derivatives are involved in enzyme-catalyzed methyl-transfer reactions.<sup>2</sup> The reaction involving *S*-adenosyl-L-methionine occurs with complete sulfur stereoselectivity.<sup>3</sup> Despite the growing interest in natural, chiral, or prochiral sulfonium compounds, access to optically active alkylsulfonium ions is very limited. So far stereospecific synthesis has been achieved only in one case, where hazardous Cd alkyls or Grignard reagents were employed with optically active sulfoxide.<sup>4</sup> Also, unequivocal information about the absolute configuration of trialkylsulfonium ions is still outstanding.<sup>5</sup> This paper presents an example of a highly stereospecific intramolecular alkylation of a dialkyl sulfide to give an optically active cyclic trialkylsulfonium tosylate whose absolute configuration was confirmed by single-crystal X-ray analysis.

(*S*)-*tert*-Butyl 2-(1-tosyloxy-4-methylthio)butylcarbamate (**1**)<sup>6</sup> was prepared starting from *N*-Boc-(*S*)-methionine ethyl ester.<sup>7</sup>

(1) (a) Kjaer, A. *Tetrahedron* **1974**, *30*, 1551. (b) Challenger, F. "Aspects of the Organic Chemistry of Sulphur"; Butterworths: London, 1959.

(2) Klee, W. A. In "Transmethylation and Methionine Biosynthesis", Shapiro, F., Ed.; The University of Chicago Press: Chicago, 1965; p 220.

(3) De La Haba, G.; Jamieson, G. A.; Mudd, S. H.; Richards, H. H. *J. Am. Chem. Soc.* **1959**, *81*, 3975.

(4) Andersen, K. K.; Caret, R. L.; Ladd, D. L. *J. Org. Chem.* **1976**, *41*, 3096. Andersen, K. K. *J. Chem. Soc. D* **1971**, 1051.

(5) Only a few examples are available: (a) Kelstrup, E.; Kjaer, A.; Abrahamsson, S.; Dahlen, B. *J. Chem. Soc., Chem. Commun.* **1975**, 629. (b) Cornforth, J. W.; Reichard, S. A.; Talalay, P.; Carrell, H. L.; Glusker, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 7292.

(6) **1**: mp 71-72 °C;  $[\alpha]_D^{20}$  -18.8° (*c* 0.76,  $\text{CHCl}_3$ ); IR (Nujol) 3352, 1678, 1595, 1508, 1242, 1169, 976, 856, 837, 810  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$  with  $\text{Me}_4\text{Si}$ )  $\delta$  1.39 (s, 9 H, *t*-Bu), 1.73 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{CH}$ ), 2.03 (s, 3 H,  $\text{SCH}_3$ ), 2.41 (s, 3H,  $-\text{C}_6\text{H}_4\text{CH}_3$ ), ~2.41 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{S}$ ), 3.87 (m, 1 H,  $-\text{CH}-$ ), 4.00 (d,  $J = 2.5$  Hz, 2 H,  $-\text{CH}_2\text{O}-$ ), 4.64 (br, 1 H, NH), 7.26 (d,  $J = 12$  Hz, 2 H, aromatic), 7.70 (d,  $J = 12$  Hz, 2 H, aromatic). Anal. Calcd for  $\text{C}_{19}\text{H}_{27}\text{NS}_2\text{O}_5$ : C, 52.42; H, 6.99; N, 3.60; S, 16.46. Found: C, 52.31; H, 6.96; N, 3.68; S, 16.42.

(7) *N*-Boc-(*S*)-methionine ethyl ester was prepared as a pale yellow oil from (*S*)-methionine ethyl ester *p*-toluenesulfonic acid salt<sup>8</sup> by reaction with *tert*-butyl 4,6-dimethyl-2-pyrimidyl thiocarbonate<sup>9</sup> and converted to the alcohol, (*S*)-*tert*-butyl 2-(1-hydroxy-4-methylthio)butylcarbamate, without purification, by treatment with  $\text{LiAlH}_4$  in THF at 40 °C (71% yield): mp 44-46 °C;  $[\alpha]_D^{20}$  -11.4° (*c* 3.0,  $\text{CHCl}_3$ ); IR (Nujol) 3400, 3350, 1680, 1513, 1389, 1375, 1363, 1322, 1300, 1290, 1262, 1240, 1164, 1096, 1072, 1059, 1035, 1015, 1004, 970, 880, 862, 850, 784  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$  with  $\text{Me}_4\text{Si}$ )  $\delta$  1.43 (s, 9 H, *t*-Bu), 1.66-2.00 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{CH}$ ), 2.10 (s, 3 H,  $\text{SCH}_3$ ), 2.40-2.68 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{S}$ ), 3.11-3.36 (m, 1 H,  $-\text{CH}-$ ), 3.42-3.85 (m, 3 H,  $-\text{CH}_2\text{O}-$  + OH), 4.99 (br d,  $J = 8$  Hz, 1 H, NH). Anal. Calcd for  $\text{C}_{10}\text{H}_{21}\text{NO}_5\text{S}$ : C, 51.04; H, 8.92; N, 5.95; S, 13.62. Found: C, 50.76; H, 8.92; N, 6.21; S, 13.50.