

It has been suggested that such effects are indicative of a *rate controlling* homolytic, or heterolytic, cleavage of the C-leaving group bond.³ Inverse effects of similar magnitude may be obtained when the reaction involves the reverse process: trigonal to tetrahedral carbon.⁴ These effects have served as a tool in ascertaining the one-step or two-step nature of decompositions of dialkyl azo compounds^{3,5} and a Diels-Alder adduct,⁶ and in the addition of diphenylketene to cyclohexene.⁷

These isotope effects have been described in terms of vibrational frequency changes from starting to transition state as the reacting carbon atom changes hybridization⁸

$$k_H/k_D = be^{0.171\sum(\nu_{H,i} - \nu_{H,i}^*)/T}$$

where b is relatively constant over small temperature ranges, $\nu_{H,i}$ is the i th C-H fundamental vibrational frequency in the starting state, $\nu_{H,i}^*$ the corresponding vibration in the transition state, and T is the absolute temperature. A net lowering of the sum of the frequencies results in $k_H/k_D > 1$.

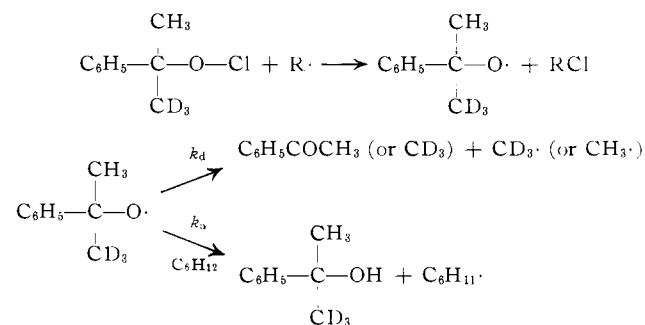
A definite exception to the pattern of $k_H/k_D \cong 1.15$ for unimolecular homolytic or heterolytic bond cleavage is the small *inverse* effect observed in the formation of methyl radicals from gas phase pyrolysis of dimethylmercury; total $k_H/k_D = 0.92$ for the fully deuterated compound.⁹ This exception led to the suggestion that the secondary α -deuterium isotope effect may be an ambiguous criterion.¹⁰

We undertook the determination of the α -deuterium isotope effect in the formation of methyl radicals by carbon-carbon rather than carbon-mercury bond cleavage. The compound chosen was methyltrideuteriomethylphenylcarbinyl hypochlorite, whose decomposition has been studied.¹¹ It was prepared *via* the alcohol from acetophenone- d_3 and a twofold excess of methylmagnesium iodide. The possibility of deuterium exchange during acid hydrolysis of $C_6H_5C(CH_3)(CD_3)OMgI$ was investigated by n.m.r. and none was found. Analysis of the alcohol for deuterium showed greater than 99% deuteration of one methyl group. The hypochlorite was obtained in high yield from the alcohol by treatment with a twofold excess of HOCl in the usual fashion.^{11b} Mass spectrometry indicated that 1.3% of the deuterated methyl group was $-CD_2H$ and all data were corrected for its presence.

The hypochlorite was irradiated by an incandescent lamp as a 0.5 M solution in carbon tetrachloride in the presence of cyclohexane (1.0 M); under these conditions the decomposition is a long chain reaction and complicating side reactions amount to less than 0.5% by gas-liquid chromatography (g.l.c.).

Path d leads to the formation of $CH_3\cdot$ and $CD_3\cdot$ in direct competition and $CH_3Cl/CD_3Cl = k_H/k_D$ for three deuterium atoms. The evolved mixture of

methyl chlorides was purified by g.l.c. and analyzed by a Consolidated-Nier mass spectrometer used as a single collector. The spectrometer was calibrated for the relative sensitivity to the two compounds with standard mixtures of CH_3Cl and CD_3Cl . For equimolar mixtures the spectrometer ratio CH_3Cl/CD_3Cl was 1.01 ± 0.01 from the 52 and 55 peaks. A correction factor of 1.45 has been reported on the basis of the 50 and 53 peaks.¹² We find 1.00 ± 0.04 in our mass



spectrometer for this ratio. The isotope effect was determined at temperatures between -9° and 75° and the results are shown in Table I. A plot of $\log(k_H/k_D)$ vs. $1/T$ gave a good straight line relationship indicating a fairly constant pre-exponential term; $b = 0.93 \pm 0.02$ for three deuterium atoms. From the slope a net decrease of 270 ± 5 cm^{-1} is obtained for the frequency changes from starting to transition state. A net decrease of about 400 cm^{-1} can be calculated for the formation of a fully formed methyl radical with a tricoordinated sp^2 carbon atom.¹³ The experimentally determined change indicates that well over half of the vibrational changes accompanying the formation of the methyl radical have occurred in the transition state. The conclusion that the transition state is more akin to products than to reactants in this reaction, involving carbon-carbon bond cleavage and the formation of a methyl radical and a double bond, is consistent with the findings of Szwarc and co-workers^{1c}; they have concluded that the transition state for methyl radical addition to olefins is closer to the configuration of the reactants than to that of the products.

TABLE I

 α -DEUTERIUM ISOTOPE EFFECT IN METHYL RADICAL FORMATION

Temp., °C.	CH_3Cl/CD_3Cl^a	k_H/k_D^b
-9	1.588 ± 0.005	1.17 ± 0.01
20	1.486 ± 0.03	1.14 ± 0.01
50	1.429 ± 0.01	1.13 ± 0.01
75	1.401 ± 0.005	1.12 ± 0.01

^a Uncorrected for relative sensitivity. ^b Corrected values per deuterium.

The determination of the isotope effect in the pyrolysis of dimethylmercury⁹ was carried out in the gas phase at a pressure corresponding to 0.95 of the rate at the high pressure limit. Subsequent to this work, strong inverse secondary effects have been observed in the isomerization of CD_3NC at low pressures in non-

(12) G. Ghiltz, *et al.*, *J. Chem. Phys.*, **38**, 1053 (1963).

(13) The C-H bond length in methyl radical is 0.013 Å. shorter than that in methane and about equal to that of ethylene [G. Herzberg, *Proc. Roy. Soc. (London)*, **A262**, 291 (1961)]; ethylene was taken as a model for the vibrational frequencies of the methyl radical.

(3) S. Seltzer, *J. Am. Chem. Soc.*, **83**, 2625 (1961).
 (4) (a) S. Seltzer, *ibid.*, **83**, 1861 (1961); (b) D. B. Denney and N. Tunkel, *Chem. Ind. (London)*, 1383 (1959); (c) however, see M. Feld, A. P. Stefani, and M. Szwarc, *J. Am. Chem. Soc.*, **84**, 4451 (1962).
 (5) S. Seltzer, *ibid.*, **85**, 14 (1963).
 (6) S. Seltzer, *ibid.*, **85**, 1360 (1963).
 (7) T. J. Katz and R. Dessau, *ibid.*, **85**, 2172 (1963).
 (8) (a) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949); (b) J. Bigeleisen and M. Wolfsberg, "Advances in Chemical Physics," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1958, p. 18; (c) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).
 (9) R. E. Weston, Jr., and S. Seltzer, *J. Phys. Chem.*, **66**, 2192 (1962).
 (10) M. J. Goldstein and G. L. Thayer, Jr., *J. Am. Chem. Soc.*, **85**, 2673 (1963).
 (11) (a) M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **15**, 748 (1950); (b) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1593 (1963). We thank Prof. Walling for suggesting this particular hypochlorite.

equilibrium thermal systems.¹⁴ These effects are strongly pressure dependent and become normal near the high pressure limit. This might contribute to the observed inverse effect of dimethylmercury. Effects of this type are known not to occur in solution.

The explanation for anomalous α -effects in the cleavage of the carbon-mercury bond¹⁵ is not obvious at present.

The demonstrated normal behavior of the methyl radical strengthens the usefulness and unambiguity of the secondary α -deuterium effect as a criterion for "unimolecular" cleavage.

(14) F. W. Schneider and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **85**, 2365 (1963).

(15) See also M. M. Kreevoy and B. M. Eisen, *J. Org. Chem.*, **28**, 2104 (1963).

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New Types of Organosulfur Derivatives of Metal Carbonyls¹

Sir:

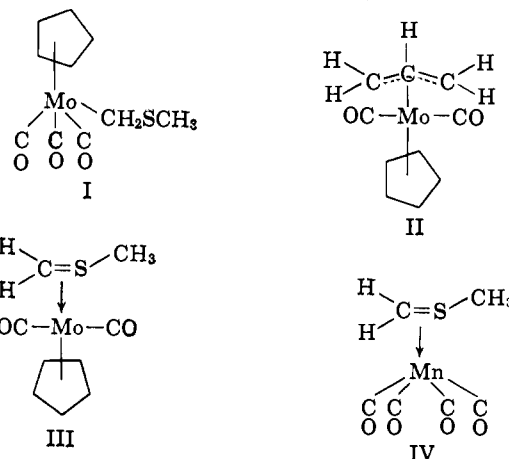
Numerous unusual organosulfur transition metal compounds have been obtained by reactions of various metal carbonyls and cyclopentadienylmetal carbonyls with certain mercaptans, sulfides, disulfides, and dithietenes.^{2,3} Other types of organosulfur transition metal compounds have been obtained from metal sulfides and certain acetylene derivatives.⁴ This communication describes a new and entirely different synthesis of new types of organosulfur derivatives of metal carbonyls with metal-sulfur bonds. These new compounds have been obtained by thermal or photochemical decarbonylation of compounds of general formula $\text{CH}_3\text{S}(\text{CH}_2)_n\text{M}(\text{CO})_x(\text{C}_5\text{H}_5)_y$ ($n = 1, 2$, or 3 ; $\text{M} = \text{Fe}$ [$x = 2, y = 1$], Mo [$x = 3, y = 1$], or Mn [$x = 5, y = 0$]) without metal-sulfur bonds. These sulfur-containing transition metal alkyl derivatives, none of which has been previously reported, may in turn be obtained from metal carbonyl anions and the chloroalkyl methyl sulfides $\text{CH}_3\text{S}(\text{CH}_2)_n\text{Cl}$.

Thus, the sodium salt $\text{NaMo}(\text{CO})_3\text{C}_5\text{H}_5$ ⁵ reacts with chloromethyl methyl sulfide in tetrahydrofuran solution at 25° to give the yellow crystalline alkyl tricarbonyl derivative $\text{CH}_3\text{SCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ (I), m.p. 66–67°. On heating to ~70° or ultraviolet irradiation this tricarbonyl derivative forms the likewise yellow crystalline dicarbonyl derivative $\text{CH}_3\text{SCH}_2\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5$ in up to 60% yield, m.p. 66–67°.^{6,7}

The infrared⁸ and proton n.m.r. spectra⁸ and close analogies in stoichiometry, physical properties, and general method of preparation to π -cyclopentadienyl- π -allylmolybdenum dicarbonyl (II)⁹ lead us to propose structure III for the dicarbonyl derivative CH_3SCH_2 -

$\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5$. In structure III a carbon-sulfur double bond is π -bonded to the molybdenum atom and the neutral CH_3SCH_2 group donates three electrons¹⁰ to the molybdenum atom in a similar manner to the π -allyl ligand. The relationship between the metal-ligand bonding in $\text{CH}_3\text{SCH}_2\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5$ (III) and the π -allyl derivative (II) is very similar to the relationship between the metal-ligand bonding in benzene-chromium tricarbonyl and thiophene-chromium tricarbonyl¹¹ and is a further demonstration of the well-known analogy between the groupings $>\text{C}=\text{C}<$ and $>\ddot{\text{S}}:$.

A similar yellow liquid manganese derivative $\text{CH}_3\text{SCH}_2\text{Mn}(\text{CO})_4$ (IV) has been obtained from $\text{NaMn}(\text{CO})_5$ and chloromethyl methyl sulfide at ~65°.⁶



Analogous experiments with 2-chloroethyl methyl sulfide¹² and various metal carbonyl anions led to some surprising results. Thus, treatment of $\text{NaMn}(\text{CO})_5$ with 2-chloroethyl methyl sulfide in boiling tetrahydrofuran gave a 26% yield of pale yellow diamagnetic¹³ crystalline volatile $\text{CH}_3\text{SCH}_2\text{CH}_2\text{Mn}(\text{CO})_5$, m.p. 56.5–58.5°. The infrared spectrum of this new organomanganese compound besides very strong bands at 2071, 1996, and 1972 cm^{-1} due to the terminal metal carbonyl groups exhibits a very strong band at 1622 cm^{-1} , which may be assigned to an acyl carbonyl group suggesting structure VI rather than structure V.

Reaction between $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ ⁵ and 2-chloroethyl methyl sulfide in tetrahydrofuran solution at room temperature yields a rather unstable orange liquid indicated by analysis and other properties to be $\text{CH}_3\text{SCH}_2\text{CH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ (VII). Ultraviolet irradiation of this material in benzene solution gives a complex mixture from which the following compounds can be isolated by chromatography on alumina in benzene solution followed by crystallization from pentane or ethanol of the fractions thus obtained: (1) unchanged $\text{CH}_3\text{SCH}_2\text{CH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$; (2) brown crystalline $[\text{CH}_3\text{SFeCOC}_5\text{H}_5]_2$ ⁶ (VIII) identical with the compound of this composition previously isolated in low yield¹⁴ from the reaction between $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$

(1) This work was supported in part by Grant AF-AFOSR-580-64 from the Air Force Office of Scientific Research.

(2) R. B. King, *J. Am. Chem. Soc.*, **85**, 1587 (1963), and references to previous work from various research groups cited therein.

(3) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, in press.

(4) G. N. Schrauzer and V. Mayweg, *J. Am. Chem. Soc.*, **84**, 3221 (1962).

(5) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1955).

(6) These compounds gave satisfactory analyses for three to six elements. Detailed analytical data will be given in the full paper.

(7) A mixture of ~25% $\text{CH}_3\text{SCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ and ~75% $\text{CH}_3\text{SCH}_2\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5$ exhibited a melting point of 55–60° indicating the melting point depression to be small but detectable.

(8) Details of these spectra will be given in the full paper.

(9) M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 889 (1963).

(10) Complexes III and IV may possibly be regarded as derivatives of the unsaturated sulfonium ion $\text{H}_2\text{C}=\text{S}-\text{CH}_3$ where the carbon-sulfur double bond is π -bonded to the transition metal like a carbon-carbon double bond.

(11) E. O. Fischer and K. Öfele, *Ber.*, **91**, 2395 (1958).

(12) Although we have experienced no difficulties in handling 2-chloroethyl methyl sulfide apart from the usual obnoxious odor of divalent sulfur compounds, we advise caution in handling this compound due to its probable high toxicity based on its close chemical relationship to bis(2-chloroethyl) sulfide, highly toxic "mustard gas."

(13) From the proton n.m.r. spectrum.

(14) An improved preparation of $[\text{CH}_3\text{SFeCOC}_5\text{H}_5]_2$ from $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ and dimethyl disulfide giving a 37% yield rather than a 9% yield has been developed and will be described in the full paper.