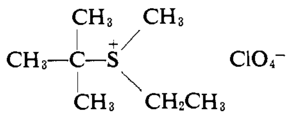
There are two mechanisms which would account for the racemization. These are (i) heterolytic carbon–sulfur bond cleavage to yield a *t*-butyl cation–ethyl methyl sulfide ion neutral molecule pair which could return to racemic sulfonium salt or react with the solvent to yield products, and (ii) inversion about the central sulfur atom analogous to the inversion of an ammonia molecule.

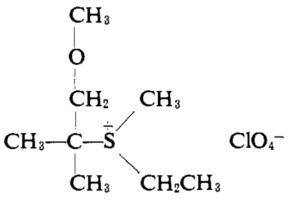
The first mechanism would represent an example of the detection of ion–neutral molecule pair return during solvolysis by racemization of the leaving group analogous to the detection of ion-pair return in solvolysis of neutral molecules by racemization of an optically active leaving group. Such a process has been at least formally demonstrated to occur in the diastereoisomer interconversion observed[6] on solvolysis of α-phenylethyl 2,6-dimethylbenzenesulfinate.

A distinction between the two mechanisms can be made on the basis of the effect of substituents upon the reaction. If the first mechanism obtains, then replacement of a hydrogen on one of the methyls of the *t*-butyl group by an electron-withdrawing substituent should, to a first approximation, slow down the heterolysis rate and hence reduce the rates of racemization and solvolysis by similar amounts. An electron-donating substituent should accelerate both the racemization and solvolysis reactions by both electronic and steric effects. If mechanism ii describes the racemization process, then any substituent introduced into the *t*-butyl group should speed up racemization by a steric effect or leave the racemization process essentially unchanged in rate.

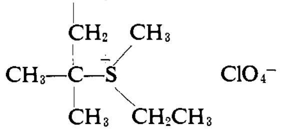
(1-Methoxy-2-methyl-2-propyl)ethylmethylsulfonium perchlorate (II), mp 102°, $[\alpha]^{25}D$ −13.5° (*c* 0.64, ethanol), and *t*-amylethylmethylsulfonium perchlorate (III), mp 137° dec, $[\alpha]^{25}D$ −25.1° (*c* 0.43, methanol), were prepared.



I



II

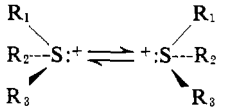


III

The relative rates of ethanolysis at 50° of compounds I:II:III are 1:0.06:6.3. These relative rates show the decrease and increase in rate expected for a heterolytic cleavage in which an electron-withdrawing and electron-donating group, respectively, are introduced as a substituent on the *t*-butyl group.

In contrast the relative rates of racemization in ethanol at 50° of compounds I:II:III are 1:1.7:3.8. The replacement of a hydrogen of the *t*-butyl group by a substituent accelerates racemization whether the substituent is electron donating or electron withdrawing. This effect cannot be electronic in origin and instead must be associated with an increase in the nonbonded interactions in the ground state relative to the transition state for racemization on introduction of the substituent. Kincaid and Henriques previously suggested[7] that as the groups attached to the central sulfur of sulfonium salts became larger such nonbonded interactions would increase the inversion rate.

The results indicate that the racemization process is best described as involving an inversion as shown below. One cannot rule out the possibility that some of the racemization of I is proceeding by mechanism i, but the major pathway for racemization must be independent of heterolysis. If this interpretation is correct it represents the first examples of the racemization of sulfonium salts by inversion.



The thermal racemization of sulfoxides is well known.[8] Mislow and co-workers[8] have suggested that many of these systems undergo racemization by a pyramidal inversion mechanism. The difference in racemization rates between the sulfonium salts here reported and the sulfoxides must arise from a combination of steric and electronic effects.

---

(6) D. Darwish and R. A. McLaren, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964, Abstracts, p 45S.

(7) J. F. Kincaid and F. C. Henriques, Jr., *J. Am. Chem. Soc.*, **62**, 1474 (1940).

(8) D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *ibid.*, **88**, 3138 (1966), and references cited therein.

(9) National Research Council of Canada Scholarship holder, 1963–1966.

David Darwish, Guy Tourigny[9]
Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada

Received August 1, 1966

Reaction of Copper(I) Chloride with Carbon Tetrachloride in Dimethyl Sulfoxide

Sir:

In previous work from our laboratory,[1] there was reported the rapid formation of copper(I) chloride by the action of copper(I) ion (in the form of the perchlorate) on carbon tetrachloride in 2-butanol containing small but significant amounts of water. In order to gain a better insight into the nature of the reaction of copper(I) ion with carbon tetrachloride, the system copper(I) chloride–carbon tetrachloride–dimethyl sulfoxide was chosen for study. This system permitted the realization of a more nearly anhydrous condition than existed previously since the source of the copper(I) could be prepared pure and anhydrous. Dimethyl sulfoxide was chosen as the medium for reaction because of its ability to dissolve copper(I) chloride. Surprisingly, when carbon tetrachloride was injected into a solution of copper(I) chloride in dimethyl sulfoxide, an almost instantaneous and copious evolution of carbon dioxide was observed. In addition some carbon monoxide was also formed. It soon became evident that copper(I) was oxidized to the dipositive

---

(1) I. V. Nelson, R. T. Iwamoto, and J. Kleinberg, *J. Am. Chem. Soc.*, **86**, 364 (1964).

state and that there was a definite relationship between the extent of this reaction, the amount of carbon dioxide formed, and the quantity of chloride ion released from carbon tetrachloride. This preliminary communication describes the unusual and unexpected results obtained.

In each experiment, carbon tetrachloride was introduced into a solution of copper(I) chloride in dimethyl sulfoxide contained in a reaction vessel which was connected to an appropriate analytical train, the whole assembly being constantly swept out with pure dry nitrogen. The flow of nitrogen was continued for periods varying from 0.5 to 12 hr after addition of the carbon tetrachloride. In Table I a summary of the quantitative information obtained in 4-hr runs is given. The mixture of carbon dioxide and monoxide was converted completely to the dioxide by passage through a tower of iodine(V) oxide, followed by absorption in 1 *M* sodium hydroxide and potentiometric titration. The reaction mixture was diluted to a definite volume, and aliquots were appropriately treated and analyzed for chloride ion by potentiometric titration with standard silver nitrate solution and for copper(II) by iodometry.

Table I. Reaction of Dimethyl Sulfoxide Solutions of CuCl with CCl_4[a]

CuCl, mmoles	Cu(II) formed, mmoles	Final Cl^-, mmoles	CO_2, mmoles	CCl_4, mmoles
2.31	1.20	3.20	0.32	5.0
2.24	1.15	3.47	0.29	5.0
6.05	3.12	9.02	0.73	5.0
6.60	3.33	9.66	0.91	5.0
6.09	3.08	8.85	0.73	5.0
10.14	5.07	14.85	1.25	5.0
10.08	5.21	14.69	1.26	5.0
10.42		14.34		1.00
10.66	3.98			1.00
18.82		23.04		1.00
19.56	3.96			1.00
9.29			0.71	1.00
10.20	4.17	13.85	0.84	1.00
19.89			0.63	1.00

[a] In each experiment, 5 ml of dimethyl sulfoxide was used and reaction was carried out at room temperature for 4 hr.

Examination of the data from those experiments in which 5 mmoles of carbon tetrachloride was used reveals a number of interesting points: (*a*) *half of the copper(I) initially present is converted to the dipositive state;* (*b*) *for each copper(II) ion formed one chloride ion is produced from carbon tetrachloride;* (*c*) *the total amount of carbon dioxide obtained is one-fourth of the quantity of copper(I) consumed or copper(II) formed; and* (*d*) *the increase in chloride ion content as a result of reaction is four times the amount of carbon dioxide obtained.* These results suggest the following over-all reactions:

$$8\mathrm{CuCl} + \mathrm{CCl_4} + \mathrm{(CH_3)_2SO} \longrightarrow (4\mathrm{Cu^I} + 4\mathrm{Cu^{II}} + 12\mathrm{Cl^-}) + \mathrm{CO} + \mathrm{(CH_3)_2S} \quad (1)$$

$$\mathrm{CO} + \mathrm{(CH_3)_2SO} \longrightarrow \mathrm{CO_2} + \mathrm{(CH_3)_2S} \quad (2)$$

It is conceivable that the precursor of the carbon monoxide is phosgene

$$8\mathrm{CuCl} + \mathrm{CCl_4} + \mathrm{(CH_3)_2SO} \longrightarrow (6\mathrm{Cu^I} + 2\mathrm{Cu^{II}} + 10\mathrm{Cl^-}) + \mathrm{COCl_2} + \mathrm{(CH_3)_2S}$$

and that this compound reacts further with copper(I)

$$2\mathrm{Cu^I} + \mathrm{COCl_2} \longrightarrow \mathrm{CO} + 2\mathrm{Cu^{II}} + 2\mathrm{Cl^-}$$

Control experiments showed that solutions of phosgene in dimethyl sulfoxide react with copper(I) chloride with the liberation of chloride ion and oxides of carbon.

The participation of dimethyl sulfoxide as a reactant was demonstrated by the presence of dimethyl sulfide in the reaction mixture. Moreover, in a control it was shown that carbon monoxide is rapidly oxidized to the dioxide by dimethyl sulfoxide at room temperature.

Points b, c, and d cited above show unequivocally that any carbon tetrachloride attacked is completely converted to a mixture of carbon monoxide and dioxide. (Analysis of the gaseous mixture in a number of instances showed the ratio of dioxide to monoxide to be approximately 9:1.) Consistent with this are the results obtained in experiments in which 1 mmole of carbon tetrachloride was used. Only that amount of copper(I) required for complete consumption of carbon tetrachloride (4 mmoles of CuCl:1 mmole of CCl_4) was oxidized to copper(II). The increase in chloride ion (*ca.* 4 mmoles) is that expected from the complete removal of halogen from carbon tetrachloride. Finally, although the quantity of carbon dioxide obtained is only 62–84% of that expected, no carbon tetrachloride was detectable by a gas chromatographic analytical technique capable of detecting at least 2% of the compound.

The utilization, in experiments in which an excess (5 mmoles) of carbon tetrachloride was employed, of only half of the copper(I) present initially is undoubtedly governed by the relative order of stability of the copper(II) chloride and copper(I) chloride species which can be formed in dimethyl sulfoxide. The reduction potential of this mixture ($\mathrm{Cu^ICl}_n{}^{+1-n}$, $\mathrm{Cu^{II}Cl}_{3-n}{}^{-1+n}$) must be sufficiently positive that copper(I) can no longer reduce carbon tetrachloride. In the absence of appropriate information, we do not feel that we can, at present, commit ourselves regarding the nature of the copper species present after reaction.

Acknowledgment. R. R. L. expresses his appreciation to the National Science Foundation for fellowship support for part of this work.

Robert R. Lavine, Reynold T. Iwamoto, Jacob Kleinberg
Department of Chemistry, University of Kansas
Lawrence, Kansas 66044

Received July 22, 1966

Formation of Ammonia by Insertion of Molecular Nitrogen into Metal–Hydride Bonds. I. The Formation of Dimeric Dicyclopentadienyltitanium(III) Hydride as an Intermediate in the Vol'pin–Shur Nitrogen-Fixing System

Sir:

Until recently the reduction of molecular nitrogen under the mild conditions of the enzymatic nitrogen-fixing reactions was completely unparalleled by any nonenzymatic reaction of the N_2 molecule. Lately, however, among some other less efficient reaction systems, a procedure has been described by Vol'pin and