

of DM has been almost⁵ neglected in the intervening interval.

Recent evidence supports the triplet state as the ground electronic level of methylene.^{6,7} The question arises whether thermal decomposition of DM proceeds with conservation of spin angular momentum to give the singlet radical, or non-adiabatically to give triplet methylene. The latter possibility is analogous to the decomposition of isoelectronic N₂O which yields O(³P) atoms, with a rate characterized by a lowered frequency factor.⁸ Shantarovich⁵ has reported the frequency factor for DM decomposition (studied below the high pressure limit at < 500°) as 8×10^{10} sec.⁻¹, a little less than the value for N₂O.

Our results on the thermal gas phase decomposition of DM support the singlet nature of the radical product. They show that the characteristic gas phase reactions of methylene with olefins, made familiar by photolysis studies of Kistiakowsky and co-workers⁹ and others,^{10,11} may also be observed with the thermally produced radicals; DM pyrolysis is a convenient source of these radicals at intermediate temperatures, in much higher yield than is obtained by photolysis of DM at 25°. ^{7a}

Decomposition of 1:10 mixtures of DM and olefins in a seasoned Pyrex bulb gave yields which were very low at 180°, improved substantially at 250°, and increased to 35% at 380°. Results at 300° (Fig. 1) with *cis*-butene-2 indicate that activated *cis*-dimethylcyclopropane undergoes the characteristic *cis-trans* geometric isomerization¹² in competition with collisional deactivation. Added oxygen, up to 10% of the total pressure, was without effect. Extrapolation to high pressures shows that addition to the double bond is essentially stereospecific. This is indicative of singlet radicals,^{9b,11} and the correctness of the conclusion of Pearson, *et al.* The characteristic structural isomerization^{9c} to pentenes of the excited cyclopropanes, and variation with pressure, is also seen. Extrapolation to high pressures indicates ~55% of *cis*-pentene-2 from addition to the C-H bond.¹⁰ *trans*-Pentene-2 production is <2% above 20 cm., which is also indicative of the absence, or negligible production, of triplet methylene.^{7b}

We have employed an interpretation, by Kistiakowsky, *et al.*,⁹ that the variation of product proportions with pressure results from collisional deactivation of the hot cyclopropane molecules formed, rather than a recent proposal that the

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(11) P. S. Skell and R. C. Woodsworth, *ibid.*, **78**, 4496 (1956).

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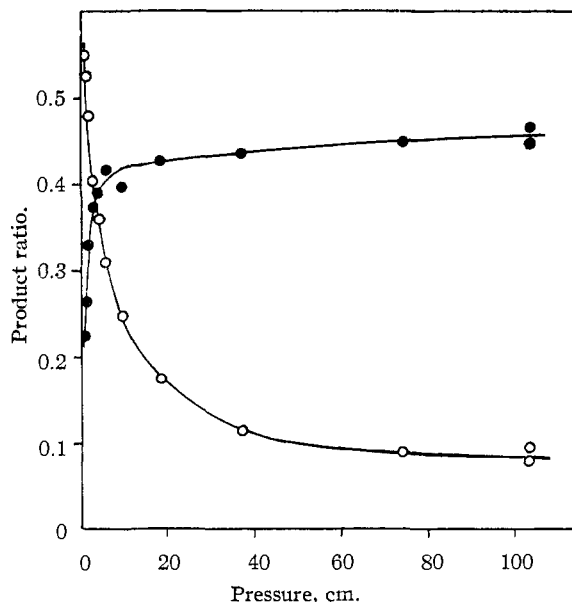


Fig. 1.—Variation of product ratios with total pressure (300°): O, dimethylcyclopropane (DMC) isomer ratios, *trans*/*(trans + cis)*; ●, DMC/(DMC + pentenes).

behavior arises from singlet-triplet transitions of methylene¹³ at lower pressures: The apparent rate constants in these systems^{9,12} are in some instances higher ($\sim 10^8$ to 10^{11} sec.⁻¹) than are known magnitudes for singlet-triplet radiative processes, or for the intersystem crossing.^{7b} In addition, different pressure dependence of the characteristic olefin formation, and of the *cis-trans* cyclopropane ratio, is observed for different substrate olefins, with the same radical source.^{9c,d,12} The different pressure dependence between olefin formation and geometric isomerization, in one and the same system,^{9d,12} also supports the present interpretation, at least at pressures above 1 cm.

The energies of dimethylcyclopropane produced in the present work, and *via* photolysis of DM,^{9d} are quite similar, as judged by relative variation of products with pressure. Studies at different temperatures may assist in better estimates of the total energy of the product species, when coupled with accurate quantum statistical calculations of rate.

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(14) N.S.F. Predoctoral Fellow.

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RECEIVED DECEMBER 5, 1960

DICHLOROFUOROMETHANESULFENYL CHLORIDE Sir:

Recently, Sheppard and Harris¹ concluded, on the basis of characteristic sulfenyl chloride reactions and fluorine magnetic resonance spectra, that the product of the fluorination of trichloromethanesulfenyl chloride, CCl₃SCl, with mercuric fluoride is dichlorofluoromethanesulfenyl chloride,

(1) W. A. Sheppard and J. F. Harris, Jr., *J. Am. Chem. Soc.*, **82**, 5106 (1960).

CFCl_2SCl , rather than trichloromethanesulfonyl fluoride, CCl_3SF , as reported by Kober.²

In the Raman spectrum of the yellow reaction product, I find that the most prominent line (532 cm.^{-1}) also occurs in the Raman spectrum of trichloromethanesulfonyl chloride (535 cm.^{-1}), where it has been assigned to the stretching vibration of the S-Cl bond.³ This observation is strong confirmatory evidence for the retention of the S-Cl bond during fluorination.

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THE ISOLATION OF ETHERATED CARBONIC ACID

Sir:

M. Schmidt¹ isolated thiosulfuric acid by the low temperature reaction of $\text{Na}_2\text{S}_2\text{O}_3$ with HCl in ether. It was thought that carbonic acid might also be prepared at low temperatures in a similar manner.

All reactions were conducted under anhydrous conditions using anhydrous reagents. Finely divided NaHCO_3 was dispersed in ether and cooled to -30° . Freshly prepared HCl in ether, also at -30° , then was added with stirring to an excess of this mixture. The addition was not accompanied by gas evolution. Analysis of a sample of the ether did not show the presence of chloride ions.

The cold ether solution was decanted from the solids, consisting of unreacted NaHCO_3 and product NaCl, and cooled to -78° . At this temperature white, snow-like crystals were precipitated slowly from solution. They began to decompose rapidly at -10° with evolution of carbon dioxide and formation of water (ice).

Quantities of this product were allowed to decompose and the products of decomposition allowed to pass through two weighed U-tubes containing anhydrous $\text{Mg}(\text{ClO}_4)_2$ and soda lime, respectively. The molar ratio of the decomposition products, namely, H_2O and CO_2 , was thus established as being approximately 1:1.

A U-tube fitted with a fritted-glass filter and which could be disconnected below the disk was used to determine the extent of etherification of the carbonic acid at low temperatures. The joined U-tube was completely immersed in a bath kept at -78° and a quantity of the precipitated crystals was then collected onto the filter disk. They were dried by a stream of precooled nitrogen. The leg containing the dry sample was then connected to a gas-measuring buret. The carbon dioxide evolved from the decomposition of the compound on warming to room temperature was measured over mercury at constant pressure. The liquid products were weighed by difference. Corrections were made for temperature, pressure and vapor pressure of water and ether. The increase in weight corresponded to a molar quantity of water

(1) M. Schmidt, *Z. anorg. und allgem. Chem.*, **289**, 141 (1957).

(expected) plus a molar quantity of ether approximately equal to the molar quantity of carbon dioxide measured.

The analyses of two preparations are given: (1) CO_2 evolved = 24.6 ml. (0.0011 mole) corrected; weight of liquid products, $(\text{C}_2\text{H}_5)_2\text{O} + \text{H}_2\text{O}$ = 0.0938 g. corrected; weight of ether = 0.0938 g. - 0.0198 g. (weight of 0.0011 mole H_2O assumed = CO_2) = 0.0740 g. (0.0010 mole); molar ratio $\text{CO}_2:\text{Et}_2\text{O}$ = 0.0011:0.0010. (2) CO_2 evolved = 9.3 ml. (0.00041 mole) corrected; weight of liquid products, $(\text{C}_2\text{H}_5)_2\text{O} + \text{H}_2\text{O}$ = 0.0407 g. corrected; weight of ether = 0.0407 g. - 0.0074 g. (weight of 0.00041 mole H_2O assumed = CO_2) = 0.0333 g. (0.00045 mole); molar ratio $\text{CO}_2:\text{Et}_2\text{O}$ = 0.00041:0.00045.

When a stream of precooled ammonia was passed through an ether solution of the compound at -30° a voluminous white precipitate immediately formed. An infrared spectrogram of this solid was identical with one of known pure $(\text{NH}_4)_2\text{CO}_3$.

An ether solution of carbonic acid was found to react generally with strong bases to form carbonates and bicarbonates.

From these preliminary experiments it can be concluded that anhydrous carbonic acid, H_2CO_3 , may be prepared and exists in ether solution at -30° as a stable entity. As such it reacts with strong bases to form carbonates and bicarbonates. In addition, the monoetherate of carbonic acid, $\text{H}_2\text{CO}_3\cdot\text{Et}_2\text{O}$, may be precipitated from ether solution at -78° filtered and analyzed.

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STRUCTURE AND NATURE OF BONDING OF $\text{C}_5\text{H}_5\text{Co}(\text{CH}_3\text{C}_2\text{CH}_3)_2\text{CO}^1$

Sir:

The reactions of certain metal carbonyls and their derivatives with alkynes have resulted in new types of complexes²⁻¹² whose exact nature, although inferred from chemical evidence, as yet is unknown.

A single crystal X-ray investigation of one of these compounds, $\text{C}_5\text{H}_5\text{Co}(\text{CH}_3\text{C}_2\text{CH}_3)_2\text{CO}$, has yielded results of definite structural interest. This compound formed by the reaction of dimethylacetylene with $\text{C}_5\text{H}_5\text{CO}(\text{CO})_2$ was first pre-

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(6) W. Hübel and E. H. Bray, *ibid.*, **10**, 250 (1959).

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(11) W. Hübel and E. Weiss, *Chem. and Ind.*, 703 (1959).

(12) P. L. Pauson, *Proc. Chem. Soc.*, 297 (1960).