

## Gas Phase Reaction of Methylene with Methyl Chloride

Sir:

The initial step in the reaction of methylene with haloalkanes in the liquid phase has been reported to be an abstraction reaction for polyhaloalkanes<sup>1</sup> and a C-Cl insertion reaction for monochloroalkanes.<sup>2,3</sup> Some C-H insertion<sup>4</sup> reaction was also reported for the monochloroalkanes.<sup>2</sup> Photolytic decomposition of diazomethane was used as the source of methylene in the above work. Owing to the large difference between the halogen compounds these data need not necessarily be considered to be in conflict.

We wish to report some studies of the gas phase reaction of methylene with methyl chloride which show that reaction takes place predominantly by Cl abstraction and not by either C-Cl or C-H insertion reactions, as might have been expected.<sup>2,4</sup>

The experiments were performed by photolyzing<sup>5</sup> 1:10 mixtures of both ketene and diazomethane with methyl chloride in the gas phase at pressures from 1 to 150 cm. Under these conditions it has been established that the methylene radicals are predominantly in the singlet state when they undergo reaction.<sup>4,6</sup> Products were identified and quantitatively measured by conventional gas chromatographic techniques.

The principal products that were found with ketene as the source of CH<sub>2</sub> are listed in Table I. At high

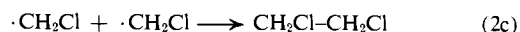
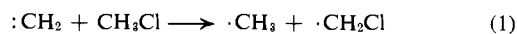
Table I. Reaction Products<sup>a</sup> of CH<sub>2</sub> with CH<sub>3</sub>Cl

Pressure, cm.	Yield, %				
	C <sub>2</sub> H <sub>6</sub> <sup>b</sup>	C <sub>2</sub> H <sub>5</sub> Cl	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	C <sub>2</sub> H <sub>4</sub> <sup>c</sup>	C <sub>2</sub> H <sub>2</sub> Cl
150	29	45	26	...	...
150	30	42	28	...	...
150	33	42	25	...	...
76	28	44	28	Trace	...
69	28	43	29	Trace	...
32	31	31	26	12	Trace
12	34	13	25	26	2
4.8	32	5	24	33	6
2.3	20	2	19	47	12
0.9	17	..	13	50	20

<sup>a</sup> Additional data not included here were used for calculation of  $k_a$  and  $k_a'$ . <sup>b</sup> Owing to slight contamination of the ketene by ethane, these analyses are less reliable than for the other products; the apparent decrease in ethane yield at pressures of less than 4 cm. has not been fully investigated and is not essential to the main ideas presented here. <sup>c</sup> The reaction of CH<sub>2</sub> with ketene generates some C<sub>2</sub>H<sub>4</sub>. This contribution to the ethylene has been subtracted out.

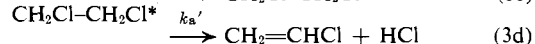
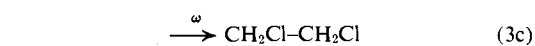
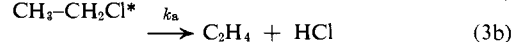
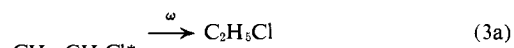
pressure, above 60 cm., the major products are ethane, chloroethane, and 1,2-dichloroethane. Experiments with diazomethane give very similar results except that side reactions are somewhat more prevalent. The pressure dependence of the two systems is nearly identi-

cal. These products are consistent with the following set of reactions.



Methylene first abstracts a chlorine atom, and then the methyl and chloromethyl undergo efficient radical combination to give ethane, chloroethane, and 1,2-dichloroethane. These products could also be consistent with C-H abstraction as the initial reaction of CH<sub>2</sub>. This possibility was checked by experiments with dichloromethane; concomitant C-H abstraction would give ethane, 1,1-dichloroethane, 1,1,2-trichloroethane, chloroethane, and 1,1,2,2-tetrachloroethane in addition to 1,2-dichloroethane as reaction products. Only the 1,2-dichloroethane was produced in significant quantities, although these other products were present in amounts indicating 20-30% C-H abstraction.

Reactions 2a-c are exothermic by an amount equal to the respective C-C bond dissociation energies, which lie between 80 and 85 kcal. mole<sup>-1</sup>. In reactions 3a-d an asterisk is used to denote this vibrational excitation. At sufficiently low pressures these molecules may undergo unimolecular decomposition. The only mode of reaction for ethane is dissociation. At 25° this is not believed to be an important reaction at pressures above 1 cm.<sup>7</sup> However, both chloroethane and 1,2-dichloroethane have a unimolecular decomposition path of lower critical energy than dissociation: the splitting out of HCl and formation of the corresponding olefin<sup>8</sup> (reactions 3b and 3d). The critical energy requirement is about 60 kcal. mole<sup>-1</sup>, compared to about 80 kcal. mole<sup>-1</sup> for dissociation. Reactions 3a and 3c represent collisional stabilization;  $\omega$  is the collision frequency.



The HCl reacts rapidly with the ketene or diazomethane<sup>9</sup> to produce acetyl chloride and methyl chloride, respectively.

Reactions 3 thus explain the increase in ethylene and vinyl chloride yields and decrease of chloroethane and 1,2-dichloroethane yields as the pressure is lowered. The apparent rate constants for 3b and 3d can be defined<sup>7</sup> as  $k_a = \omega(\text{C}_2\text{H}_4/\text{C}_2\text{H}_5\text{Cl})$  and  $k_a' = \omega(\text{C}_2\text{H}_3\text{Cl}/\text{C}_2\text{H}_4\text{Cl}_2)$ . Numerical values derived from our preliminary data in pressure units of cm. give  $k_a \sim 20$  and  $k_a' \sim 1.9$ . These rate constants are independent of the two sources of methylene used in this work; since methylene from these two sources contains different quantities of excess energy,<sup>4</sup> which would be incorporated into the chloroethane molecules by insertion but probably not by the abstraction mechanism, this is further support for the latter mechanism.

(7) B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.*, **3**, 53 (1964).

(8) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 258.

(9) J. C. Hassler and D. W. Setser, *J. Am. Chem. Soc.*, submitted.

(1) W. H. Urry and N. Bilow, *J. Am. Chem. Soc.*, **86**, 1815 (1964); W. H. Urry, J. R. Eiszner, and J. W. Wilt, *ibid.*, **79**, 918 (1957).

(2) J. N. Bradley and A. Ledwith, *J. Chem. Soc.*, 1495 (1961).

(3) V. Franzen, *Ann.*, **627**, 22 (1959).

(4) For summaries of methylene radical reactions, see (a) H. M. Frey, *Progr. Reaction Kinetics*, **2**, 131 (1964); (b) W. B. DeMore and S. W. Benson, *Advan. Photochem.*, **2**, 219 (1964).

(5) Ketene was photolyzed with  $\sim 3200\text{-}\text{\AA}$ . light which was obtained by passing the output of a mercury vapor AH-6 lamp through a solution of NiSO<sub>4</sub>·6H<sub>2</sub>O and CoSO<sub>4</sub>·7H<sub>2</sub>O. An interference filter was used to isolate the 4358- $\text{\AA}$ . band for the diazomethane photolysis.

(6) J. W. Simons and B. S. Rabinovitch, *J. Phys. Chem.*, **68**, 1322 (1964).

Further evidence for the abstraction mechanism was obtained by adding a few per cent oxygen to the reaction vessels. In these experiments, which were done at high pressure, the ethane, chloroethane, and 1,2-dichloroethane reaction products were virtually completely eliminated. This is true for both diazomethane and ketene as the methylene sources. It is well known that the reaction of  $O_2$  with singlet methylene is slow<sup>4,6</sup> while  $O_2$  is a good scavenger for alkyl-type radicals. Consequently these oxygen results support strongly the abstraction mechanism.

In conclusion we can set a limit from our data of less than 5% C-H or C-Cl insertion for the gas phase reaction of methylene with methyl chloride. The principal reaction is Cl abstraction; however, some H abstraction occurs concurrently. Further work is continuing with other alkyl halides with the objectives of determining the factors which govern insertion vs. abstraction reactions of  $CH_2$  as well as studying the unimolecular decomposition reactions of the vibrationally excited alkyl halides.

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## Heterocyclic Diquaternary Salts

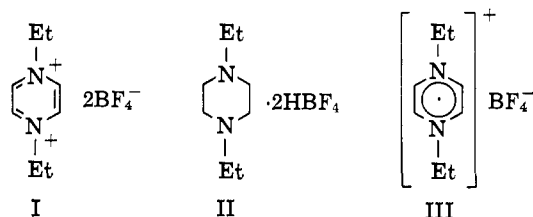
Sir:

All previous attempts to prepare diquaternary salts of pyrazines, pyrimidines, and pyridazines have apparently met with failure.<sup>1</sup> We now wish to report that both pyrazines and pyrimidines can be converted to diquaternary salts by the action of triethyloxonium fluoroborate<sup>2</sup> in refluxing dichloroethane.

The following bases have been dialkylated by this procedure (yield in parenthesis): pyrazine (97%), 2,5-dimethylpyrazine (95%), 2,6-dimethylpyrazine (46%), 2,3,5,6-tetramethylpyrazine (6%), pyrimidine (86%), and 4,6-dimethylpyrimidine (97%). The structures assigned to the alkylation products follow from elemental analyses and n.m.r. spectra,<sup>3</sup> the latter indicating the presence in every case of two equivalent ethyl groups located on nitrogen. In addition, 1,4-diethylpyrazinium difluoroborate (I) has been catalytically reduced to 1,4-diethylpiperazinium dihydrofluoroborate (II), identical in all respects with a sample prepared from authentic 1,4-diethylpiperazine and fluoroboric acid.

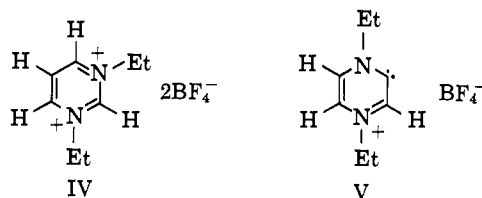
The presence of two positive charges in a conjugated ring might lead to unusual reactivity, processes resulting in net loss of a positive charge being strongly favored. In point of fact, pyrazinium and pyrimidinium di-

quaternary salts are extremely reactive substances. Alcoholic solutions of the pyrazinium salts give rise to strong e.p.r. signals. For example, a  $10^{-3}$  M solution of I in ethanol shows a complex spectrum (greater than 200 lines), analysis<sup>4</sup> of which fully supports the conclusion that the paramagnetic species present is the radical cation III. Identical e.p.r. spectra were obtained from solutions of I in methyl, ethyl, and isopropyl alcohols and, moreover, these solutions when prepared *in vacuo* showed little spectral change after 3 months. The radical cation is thus readily formed from the dication and is stable in the absence of air.



It was also possible to observe formation of III by n.m.r. techniques. When a trifluoroacetic acid solution of I in an open tube was briefly contacted with granulated zinc, the radical cation formed<sup>5</sup> caused such line broadening that virtually no n.m.r. spectrum could be observed. However, as the concentration of III decreased with time,<sup>6</sup> broad peaks began to appear and to sharpen, until after 30 min. the original spectrum had reappeared with only slightly diminished intensity.

All the pyrazinium diquaternary salts prepared thus far have yielded strong e.p.r. signals upon solution in alcohols. It seems reasonable to conclude that such facile electron abstraction is due in part to the reduction of an unfavorable charge interaction in the parent dication. One might therefore expect pyrimidinium diquaternary salts to undergo even more facile electron abstraction. We have, however, been unable to show radical cation formation from 1,3-diethylpyrimidinium difluoroborate (IV) by either of the techniques used for the analogous pyrazinium compounds. It is, of course, possible that a short-lived radical was formed in these experiments but was undetected by the techniques employed. We are currently investigating this possibility.



The facility with which the pyrazinium diquaternary salts formed radical cations suggested that they might readily lose a proton to form cation ylides, for example V. Unfortunately, attempts to exchange deuterium into the ring hydrogens of I under a variety of conditions led to decomposition without observable exchange. When, however, the analogous pyrimidinium salt IV

(1) The literature abounds with examples of alkylations in which use of a large excess of alkyl halide leads only to monoalkylation. See also: Y. T. Pratt in "Heterocyclic Compounds," Vol. 6, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1957, p. 400; C. T. Bahner and L. L. Norton, *J. Am. Chem. Soc.*, **72**, 2881 (1950); A. E. Blood and C. R. Noller, *J. Org. Chem.*, **22**, 844 (1957).

(2) H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willfang, *J. prakt. Chem.*, **154**, 83 (1939).

(3) Observed in trifluoroacetic acid.

(4) This analysis was carried out by Professor Charles Johnson of Yale University and will be reported elsewhere.

(5) That III was formed under these conditions was demonstrated by conducting the zinc reduction in a sealed evacuated tube and examining the resulting solution in the e.p.r. spectrometer. The spectrum observed was identical with that of the diquaternary salt in alcohol.

(6) Presumably due to reaction with atmospheric oxygen.