

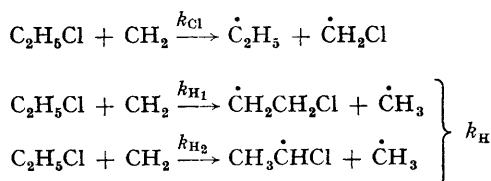
The Interaction of Methylene and Ethyl Chloride

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THE reactions between methylene and alkyl halides in the gas phase have received comparatively little attention. Setser, Littrel, and Hassler,¹ Hassler and Setser,² and Hassler, Setser, and Johnson³ have shown that with methyl chloride and methylene chloride, abstraction reactions yield mono-radicals which interact to give the observed products, and we have drawn similar conclusions from a general examination of the reactions of methylene with methyl, ethyl, n-propyl, and methylene chlorides.⁴ These reactions therefore differ from those between methylene and hydrocarbons, which appear to proceed mainly by an insertion mechanism.⁵ We have now made a detailed study of the methylene-ethyl chloride system which appears to throw new light on the reaction mechanism. As in the earlier work methylene was obtained by the photolysis of keten and the experimental details were essentially similar to those already described.⁴

Nineteen products have been identified, of which twelve have been estimated. All can be accounted for by reactions following the three primary abstraction reactions of methylene shown below.



The insertion products are n- and iso-propyl chlorides, which could also arise by combination of the appropriate radicals. These molecules are formed with a considerable excess of energy, and, unless they are stabilised, decompose into propene and HCl. According to the free-radical mechanism the sum of the yields of n- and iso-propyl chlorides and propene should equal twice the combined yields of ethane and butane arising from radical recombination. This is found to hold within experimental error under all conditions; consequently we believe that in our experiments methylene insertion does not play more than a minor role in the overall process.

The ratio $k_{\text{Cl}}/k_{\text{H}}$ may be evaluated from the relative yields of butane and propane, due allowance being made for the known combination: disproportionation ratios of the radical pairs⁶

(k_{H} is the overall rate constant for hydrogen abstraction). For present purposes the effects of abstraction reactions of $\text{CH}_3\cdot$, on the ratio $(\text{C}_4\text{H}_{10})/(\text{C}_3\text{H}_8)$, which can be shown to be small, have been neglected. The dependence of $k_{\text{Cl}}/k_{\text{H}}$ on the wavelength of the photolysing light and the presence of added gases has been examined. In the experiments described the ratio $(\text{C}_2\text{H}_5\text{Cl})/(\text{CH}_2:\text{CO})$ was always 5.

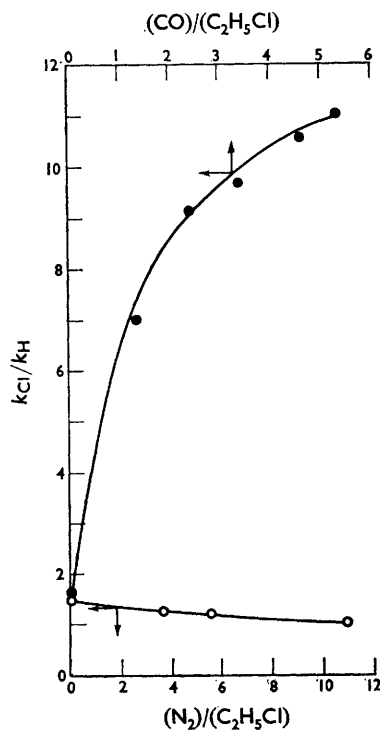


FIGURE. Dependence of $k_{\text{Cl}}/k_{\text{H}}$ on the pressure of foreign gases. Quartz optics, with full light of high-pressure mercury arc. Initial ratio $(\text{C}_2\text{H}_5\text{Cl})/(\text{CH}_2:\text{CO}) = 5$.

- initial pressure 9.8 cm., CO added
- initial pressure 4.9 cm., N₂ added.

With quartz optics and the full light of a high-pressure mercury arc, and a total pressure of 9.8 cm., we find $k_{\text{Cl}}/k_{\text{H}} = 1.6$ (in the absence of foreign gas). Removal of wavelengths shorter than 3100 Å leads to $k_{\text{Cl}}/k_{\text{H}} = 0.86$. In the presence of added nitrogen the ratio also assumes

lower values as shown in the Figure. A much more dramatic effect on $k_{\text{Cl}}/k_{\text{H}}$ is obtained if carbon monoxide is added before photolysis; in this case the ratio may be greatly increased (Figure). The yields of products other than propane and butane also show the variation expected for the changes in $k_{\text{Cl}}/k_{\text{H}}$.

We interpret these results in terms of variations in the ratio of singlet to triplet methylene, the two species having different reactivities towards C-H and C-Cl bonds. It is generally considered that the use of long wavelengths and the addition of inert gases such as N_2 increase the proportion of triplet methylene.^{7,8} On the other hand, DeGraff and Kistiakowsky⁹ have provided strong evidence that triplet methylene reacts 20 times as fast as the singlet with CO, so that addition of CO provides a means of obtaining predominantly singlet methylene. Our results indicate that the singlet abstracts chlorine predominantly; if hydrogen abstraction is confined to the 1-positions the

relative reactivities of C-Cl and C-H are in the ratio 22:1. Since some abstraction occurs from the 2-positions, and the limiting effect of CO has not been realised in the experiments in the Figure, this value is a minimum. Abstraction by triplet methylene appears to be comparatively indiscriminate; zero discrimination would correspond to $k_{\text{Cl}}/k_{\text{H}} = 0.2$. Hassler and Setser² have remarked that their findings with methylene chloride can be interpreted similarly.

This is a surprising result since from energy considerations the triplet (ground) state would be expected to be more discriminating. Probably the electronic configuration, rather than the energy, is the critical factor; the singlet might react preferentially with the chlorine atom by virtue of its empty p_z orbitals, while the triplet behaves similarly to a simple alkyl radical.

(Received, September 4th, 1967; Com. 943.)

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