

CHLORINE ATOM ABSTRACTION BY METHYL RADICALS*

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Although extensive studies have been made on the abstraction of hydrogen atoms by free radicals in the gas phase,^{1a} little work has been reported on the abstraction of halogen atoms. Phillips² has demonstrated the abstraction of chlorine atoms from gaseous *t*-butyl hypochlorite by methyl radicals. Solution studies have been reported by Evans, Fox, and Szwarc^{3,4,5} who studied halogen atom abstraction by methyl radicals from the compounds CH₃Br, CH₃I, C₂H₅I, *s*-C₃H₇I, *t*-C₄H₉I, PhCH₂Br, PhCH₂I, CH₂ClBr, CH₂ClI, CHCl₂I, CHCl₂Br, CCl₄, CCl₃Br, and CF₃I. Toluene was used as a solvent and acetyl peroxide was used as a thermal source of methyl radicals. The abstraction by methyl radicals of chlorine atoms from gaseous ethyl chloride, neopentyl chloride, and 1,2-dichloroethane is now reported here.

For these studies methyl radicals were produced by di-*t*-butyl peroxide decomposition^{1b} using a tubular forced-flow reactor with nitrogen as a carrier gas. The effluent gas containing the reaction products was sampled with a gas-tight syringe and analysed by means of gas chromatography, the initial concentration of reactant(s) being determined by sampling from a by-pass line in the flow system.

Experiments on di-*t*-butyl peroxide alone showed the reaction products to be almost entirely acetone and ethane, and the first-order rate coefficients for the decomposition (calculated from the rate expression for a gas reaction in a flow system assuming no mixing⁶) were expressible as (*E* in calories)

$$k_1 = 4.85 \times 10^{15} \exp(-38100/RT)$$

these results being in close agreement with those of other workers (see for example the results of Raley, Rust, and Vaughan,⁷ and of Mulcahy and Williams⁸).

For the halogen atom abstraction experiments mixed vapours of di-*t*-butyl peroxide and the chlorinated hydrocarbon were carried by the nitrogen stream through the tubular reactor at temperatures within the range 200–250°. An excess of chloroalkane over di-*t*-butyl peroxide was used, and the experimental conditions were

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¹ Trotman-Dickenson, A. F., "Gas Kinetics." (a) pp. 168–237; (b) p. 197. (Butterworths: London 1955.)

² Phillips, L., *Proc. Chem. Soc.*, 1961, 338.

³ Evans, F. W., Fox, R. J., and Szwarc, M., *J. Amer. Chem. Soc.*, 1960, **82**, 6414.

⁴ Evans, F. W., and Szwarc, M., *Trans. Faraday Soc.*, 1961, **57**, 1905.

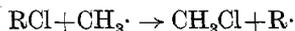
⁵ Evans, F. W., Fox, R. J., and Szwarc, M., *Trans. Faraday Soc.*, 1961, **57**, 1915.

⁶ Frost, A. A., and Pearson, R. G., "Kinetics and Mechanism." p. 263. (Wiley: New York 1961.)

⁷ Raley, J. H., Rust, F. F., and Vaughan, W. E., *J. Amer. Chem. Soc.*, 1948, **70**, 88, 1336.

⁸ Mulcahy, M. F. R., and Williams, D. J., *Aust. J. Chem.*, 1961, **14**, 534.

adjusted to give nearly complete decomposition of the peroxide. In all cases methyl chloride (as well as methane) was found to be a major reaction product, almost certainly being produced by direct abstraction by methyl radicals of chlorine atoms from the chlorinated hydrocarbons:



The proportion of ethane to acetone was considerably less than in the case of the pyrolysis of di-*t*-butyl peroxide alone, and when each of the compounds, ethyl chloride, neopentyl chloride, and 1,2-dichloroethane, was passed through the reactor under the same experimental conditions but in the absence of di-*t*-butyl peroxide there was found to be negligible decomposition.

Methyl chloride was also produced from the pyrolysis of di-*t*-butyl peroxide in the presence of *s*-propyl chloride and *t*-butyl chloride, but these experiments were less conclusive because under similar experimental conditions in the absence of the peroxide these chlorinated hydrocarbons underwent considerable decomposition to hydrogen chloride and the corresponding alkene.

Since this preliminary work was carried out* Tomkinson, Calvin, and Pritchard⁹ have reported on the abstraction of chlorine atoms from the fully chlorinated organic compounds, carbon tetrachloride, hexachloroacetone, and hexachloroethane by methyl radicals from di-*t*-butyl peroxide at 90–140°.

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⁹ Tomkinson, D. M., Calvin, J. P., and Pritchard, H. O., *J. Phys. Chem.*, 1964, **68**, 541.