plates of *N*-phenyl-*N'*-toluene-*p*-sulphonylurea (melting point 164°, decomp.) and opaque needles of *N*-phenyl-*N'*-toluene-*p*-sulphenylurea (melting point 172°, decomp.) (each in 25–35 per cent yields), together with smaller quantities of *p*-tolyl toluene-*p*-thiolsulphonate and di-*p*-tolyl disulphide. The analogous reaction with toluene-*p*-sulphenyl chloride gave the sulphenylurea and sulphonylurea in 65 and 3 per cent yields respectively. Similar results were obtained with other members of the urea series.

In their reactions with arylureas, sulphonyl and sulphenyl chlorides thus resemble halides of carbonylic acids rather than those of sulphonic acids. Further experiments in connexion with this work, particularly its extension to the thiourea-series, are in progress, and a detailed account will appear elsewhere in due course.

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¹ Walther and Włodkowski, *J. Prakt. Chem.*, **59**, 271 (1899).

² Kurzer, *J. Chem. Soc.*, 1034, 3029, 3033 (1949); 3269 (1950); 1258 (1951).

³ Oxley, Partridge, Peak, and Short, *J. Chem. Soc.*, 1514, 1618 (1948); *Chem. and Indust.*, 419 (1949).

Unimolecular Chlorohydrocarbon Decompositions

THEORIES of gaseous unimolecular reactions have often been discussed¹; but very few examples of processes occurring virtually completely by this mechanism have been used to compare theory and experiment. Thus the decompositions of azomethane, nitrous oxide and nitrogen pentoxide, which have been exhaustively examined from this point of view, are not now considered to be simple unimolecular reactions². It is desirable, therefore, to have authenticated examples, and some evidence has already been presented that the homogeneous, first-order pyrolyses of ethyl, isopropyl and *tert.* butyl chlorides and of ethylidene dichloride are of this type³. This evidence is found mainly in comparisons with the obvious radical chain-decompositions of 1,2 dichloroethane and the tetrachloroethanes⁴. In contrast with the latter, the former show no induction periods, no inhibition by propylene, little sensitivity to oxygen and chlorine, and, in the case of ethyl chloride, there is reasonable agreement between the experimental activation energy and that calculated by the semi-empirical method.

These apparently unimolecular processes are now being examined at low pressures in an apparatus essentially similar to that used previously^{3,4}. The rate-constants for the decompositions of ethyl chloride and ethylidene dichloride have been shown to fall from the high-pressure values less than $p = 6$ mm. of mercury at 456° C. and 17 mm. at 412° C. respectively. The accompanying graph illustrates the results obtained. It may be noted that at high pressures the reported rate-constants agree satisfactorily with those calculated from the rate-equations given by Barton and Howlett⁵.

The classical theory of unimolecular reactions:

$$k = \frac{A \{ \exp(-E/RT) \} (E/RT)^{s-1}}{(s-1)!}$$

●, Ethyl chloride; ▲, ethylidene dichloride. Note change of scale above 20 mm.

may be used in conjunction with the inflexion point in the curve of rate-constant against pressure to estimate the number of vibrational degrees of freedom (s) contributing towards the activation energy⁶. By assuming collision diameters of 6 Å. in each case⁶, the values of s are calculated to be 15 for ethyl chloride and 7 for ethylidene dichloride.

The order of reaction for ethylidene dichloride pyrolysis begins to rise perceptibly above unity at pressures less than 4 mm. mercury and reaches approximately 1.5 at 1 mm. pressure. Thus the evidence that these reactions are truly unimolecular is considerable. Further work is in hand and will be fully reported shortly.

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¹ Compare, for example, *Chem. Rev.*, **10**, 1 (1932), symposium on the kinetics of homogeneous reactions. Kassel, L. S., "Kinetics of Homogeneous Gas Reactions" (Chem. Catalogue Co., 1932). Hinshelwood, C. N., "Kinetics of Chemical Change" (Oxf. Univ. Press, 1940). Glasstone, S., Laidler, K. J., and Eyring, H., "Theory of Rate Processes" (McGraw-Hill, 1941).

² See Hinshelwood, C. N., *loc. cit.*, p. 124. Glasstone, G., Laidler, K. J., and Eyring, H., *loc. cit.*, p. 296. Pease, R. N., "Equilibrium and Kinetics of Gas Reactions", 129, 138 (Princeton Univ. Press, 1942). Ogg, R. A., *J. Chem. Phys.*, **15**, 337 (1947).

³ Barton, D. H. R., and Howlett, K. E., *J. Chem. Soc.*, 165 (1949). Barton, D. H. R., and Onyon, P. F., *Trans. Farad. Soc.*, **45**, 725 (1949). Barton, D. H. R., and Head, A. J., *Trans. Farad. Soc.*, **46**, 114 (1950).

⁴ Barton, D. H. R., and Howlett, K. E., *J. Chem. Soc.*, 155 (1949). Howlett, K. E., *Nature*, **165**, 860 (1950); *Trans. Farad. Soc.*, **48**, 25 (1952). Barton, D. H. R., and Howlett, K. E., *J. Chem. Soc.*, 2033 (1951).

⁵ Compare Hinshelwood, C. N., *loc. cit.*, p. 81.

⁶ Computed from the viscosity data for ethane, by analogy with the variation in the chloromethanes; see Partington, J. R., "Advanced Treatise on Physical Chemistry", 860 (Longmans, 1949).

Chlorogenic Acids in Fruit Trees

WORK on the chemical composition of the various parts of fruit trees, particularly apple and pear, is proceeding at Long Ashton and East Malling Research Stations and the Ditton Laboratory. The problems being studied are not quite the same in each laboratory, but discussions of common interests have disclosed certain overlapping findings. For this