1105. *Electrophilic Additions to Alkenes. Part I. Kinetics of the Reaction of 2,4-Dinitrobenzenesulphenyl Bromide with Cyclohexene in Acetic Acid Solution*[1]

By D. S. Campbell and D. R. Hogg

The reaction of 2,4-dinitrobenzenesulphenyl bromide with cyclohexene in acetic acid was found to be second-order, and follows a similar mechanism as that proposed for the corresponding chloride.

KINETIC studies have been reported for the reaction of 2,4-dinitrobenzenesulphenyl chloride with a variety of alkenes,[2] but no such studies have been reported for arylsulphenyl bromides. Kharasch and Havlik[3] found that the reaction of 2,4-dinitrobenzenesulphenyl bromide with *trans*-but-2-ene differed slightly from that of the corresponding chloride in requiring a definite initial pressure of the alkene before reaction occurred at an observable rate. We have studied the kinetics of the reaction of 2,4-dinitrobenzenesulphenyl bromide with cyclohexene in acetic acid solution for comparison with the results similarly obtained with the chloride,[2b] in order to confirm that the reactions follow similar mechanisms, and to obtain further evidence of the mechanism of addition of sulphenyl halides to alkenes.

2,4-Dinitrobenzenesulphenyl bromide reacts with cyclohexene in acetic acid solution to give 2-bromocyclohexyl 2,4-dinitrophenyl sulphide,[4] which was obtained pure in 98%

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[1] Presented, in part, at the XIXth Internat. Congr. Pure Appl. Chem., July 1963, London.

[2] (*a*) W. L. Orr and N. Kharasch, *J. Amer. Chem. Soc.*, 1953, **75**, 6030; 1956, **78**, 1201; (*b*) D. R. Hogg and N. Kharasch, *ibid.*, 1956, **78**, 2728; (*c*) N. Kharasch and H. H. von Duesel, *J. Org. Chem.*, 1959, **24**, 1806; N. R. Slobodkin and N. Kharasch, *J. Amer. Chem. Soc.*, 1960, **82**, 5837; H. Kwart and L. J. Miller, *ibid.*, 1961, **83**, 4552.

[3] N. Kharasch and A. J. Havlik, *J. Amer. Chem. Soc.*, 1953, **75**, 3734.

[4] C. M. Buess, N. Kharasch, and S. I. Strashun, *J. Amer. Chem. Soc.*, 1952, **74**, 3422.

yield under the conditions used for the kinetic measurements. Rates of reaction were measured dilatometrically, and also by titrating aliquot portions. The reaction, like that of the corresponding chloride, was second-order, first-order in each reactant. Values for the velocity constants at various temperatures are:

Temp.	25·0°[a]	25·0[b]	35·0[a]	45·0[a]
10^2k (l. mole^{-1} sec.$^{-1}$)	1·98	1·90	3·49	6·42

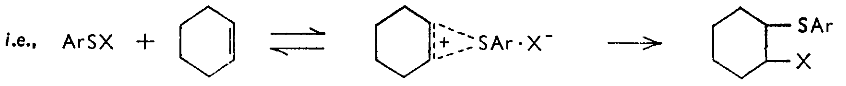
[a] Dilatometric method. [b] Aliquot portions.

The values represent the average of at least three determinations, those obtained by the dilatometric method being reproducible to within ±3%, and those by the titration method to within ±5%. Activation parameters for the bromide and chloride [2b] are tabulated below.

	10^3k (25·0°) (l. mole^{-1} sec.$^{-1}$)	E_a (kcal. mole^{-1})	$\Delta S^{\ddagger}$ (cal. deg.$^{-1}$ mole^{-1})	$\Delta G^{\ddagger}$ (kcal. mole^{-1})
ArSBr	19·8	11·2 ± 0·5	−30·7 ± 1·0	19·7
ArSCl	7·8	11·1 ± 0·5	−32·7 ± 1·0	20·3

Ar = 2,4-dinitrophenyl.

It is evident that the reaction of 2,4-dinitrobenzenesulphenyl bromide with cyclohexene in acetic acid solution follows a similar mechanism to that proposed for the corresponding chloride.[5]



X = Cl, Br.

If the first step is rate-limiting then the equality, within experimental error, of the activation parameters for these reactions may be explained by the similarity in the energies required for the heterolysis of the sulphur–chlorine and sulphur–bromine bonds. The difference in these energies, ΔG_{S-X}, is given by:

$$\Delta G_{S-X} = \Delta E_{S-X} - \Delta E_{X\cdot} - \Delta G_S(X^-)$$

Cottrell[6] gives a value of 61 kcal. mole^{-1} for the bond energy, E_{S-X}, of the sulphur–chlorine bond, and an estimate of 52 kcal. mole^{-1} for the sulphur–bromine bond. The difference in bond energies is compensated by a difference in the electron affinities, $\Delta E_{X\cdot}$, of the chlorine and bromine atoms[7] of 5·7 ± 0·2 kcal. mole^{-1}, and in the free energies of solvation, $\Delta G_S(X^-)$, of the ions in acetic acid solution, which is estimated as being slightly lower than the value of 4 kcal. mole^{-1} recorded for methanol and ethanol.[8] In the intermediate the halide ion forms part of an ion-pair, and this should further decrease $\Delta G_S(X^-)$.

If the second step is rate-limiting then the greater reactivity of the bromide, by a factor of 2·5, must be due essentially to the greater nucleophilic reactivity of the bromide ion relative to the chloride ion. This step is analogous to the reaction of halide ion with the conjugate acid of 1,2-epoxides in aqueous solution,[9] and to the reaction of halide ion with trimethylsulphonium ion in ethanol,[10] for which relative rates of 4—5 are recorded. The factor of 2·5 found in this study seems rather low for this step to be rate-limiting, although the weaker solvating power of the medium in one case and the stability of the cation would tend to decrease the difference in reactivity.

The slightly greater reactivity of the bromide in the reaction may be compared with the third-order reaction of bromine, and bromine chloride, with alkenes in acetic acid solution[11] for which the relative rates are 1 : 400, respectively. With the sulphenyl halides studied it

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[5] N. Kharasch and C. M. Buess, *J. Amer. Chem. Soc.*, 1949, **71**, 2724.
[6] T. L. Cottrell, "Strengths of Chemical Bonds," Butterworths, London, 2nd edn., p. 255.
[7] R. S. Berry and C. W. Reimann, *J. Chem. Phys.*, 1963, **38**, 1540.
[8] B. E. Conway, "Electrochemical Data," Elsevier, Amsterdam, 1952, p. 134.
[9] J. N. Brönsted, M. Kilpatrick, and M. Kilpatrick, *J. Amer. Chem. Soc.*, 1929, **51**, 428.
[10] E. D. Hughes, C. K. Ingold, and Y. Pocker, *Chem. and Ind.*, 1959, 1282.
[11] E. P. White and P. W. Robertson, *J.*, 1939, 1509.

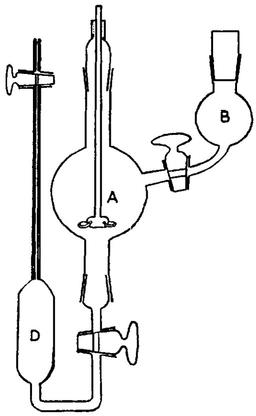
seems unlikely that the slight variation in the initial partial positive charge on the sulphur atom is important in determining the relative rates of the reactions.

It was not possible to extend this study to include the corresponding fluoride and iodide, as these compounds are unknown. Attempts to prepare 2,4-dinitrobenzenesulphenyl fluoride, and to trap the corresponding iodide are described in the Experimental section.

Experimental.—Materials. 2,4-Dinitrobenzenesulphenyl bromide,[4] m. p. 104·5—105·5°, cyclohexene,[2b] b. p. 82·5—83·0°, n_D^{20} 1·4459—1·4462, and dry acetic acid,[2a] b. p. 117·5—118·0°, n_D^{20} 1·3715—1·3718, were obtained as previously described. The liquids were redistilled in an atmosphere of nitrogen before use.

Product isolation. 2,4-Dinitrobenzenesulphenyl bromide (9·57 g.) and cyclohexene (10 g.) were dissolved in dry acetic acid (150 ml.). After 48 hr. in the dark at room temperature, the solvent and excess of cyclohexene were distilled off under reduced pressure to give a yellow crystalline residue (12·31 g.), m. p. 116—117°. Recrystallisation from benzene, and chromatography of the mother-liquors on alumina gave 2-bromocyclohexyl 2,4-dinitrophenyl sulphide (12·13 g., 98%), m. p. 120—121° (Found: C, 39·7; H, 3·8; Br, 22·0; S, 8·7; N, 7·7%. Calc. for $C_{12}H_{13}BrN_2O_4S$, C, 39·9; H, 3·6; Br, 22·1; N, 7·8; S, 8·9%).

Rate measurements. The apparatus consisted of a single-stem dilatometer, D, capacity 50 ml., internal capillary diameter 1·0 mm., connected to a mixing flask as shown. No leakage was observed at the taps under the experimental conditions. The bulb of the dilatometer was wrapped in aluminium foil to exclude light, and the apparatus placed in a thermostat-bath, with a measured temperature fluctuation of less than ±0·002° during the reaction period. Standard solutions of the reactants were prepared at the reaction temperature, and pipetted into the bulbs A and B. The solution in bulb A was vigorously stirred, and the other solution added. The starting time for the reaction was taken as the time when approximately half of the solution had been added. Stirring was continued for 2 min. before the reaction mixture was transferred to the dilatometer. Cathetometer readings of the meniscus level were recorded at one-minute intervals for the first 20 min. and then at progressively longer intervals. A constant meniscus level was obtained after 4—8 hr. The total contraction was 3—5 cm., or approximately 0·03—0·05 ml. In spite of precautions taken to ensure minimum delay between the start of the reaction and the first accurate reading, about 30% of this contraction could not be measured, and the meniscus level at zero time, l_0, could not be obtained accurately by direct extrapolation. To obtain l_0, the value $a/l_t—l_\infty$, where a is the initial concentration of the minor reactant, was plotted against time for all runs at the same temperature in the same dilatometer. Extrapolation to zero time gave $a/l_0—l_\infty$, which should be constant if the fractional change in volume per mole of reaction is constant. The value which gave the best extrapolation for all runs was chosen, and l_0 calculated. The results were calculated by the method described by Benford and Ingold,[12] and good linear plots for a second-order reaction were obtained up to 70—80% completion of reaction. The rate of reaction was also followed by taking aliquot portions, and determining the concentration of 2,4-dinitrobenzenesulphenyl bromide by the iodometric method of Kharasch and Wald.[13] This method was found to be accurate to within ±2% at concentrations of 0·01M or below, but the accuracy decreased at higher concentrations, the values generally being low. The spread of individual points was greater with this method than with the dilatometric method. Velocity constants were calculated from the slopes of the linear plots for the second-order reaction. The observed variation of sulphenyl bromide concentration with time, and the curve calculated from the velocity constant and initial concentrations of reactants showed excellent agreement to over 90% reaction. Possible variation of the velocity constant with initial reaction concentration could not be explored beyond concentrations of 0·02—0·05M in 2,4-dinitrobenzenesulphenyl bromide and 0·02—0·075M in cyclohexene owing to experimental difficulties.



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[12] G. A. Benford and C. K. Ingold, *J.*, 1938, 929.

[13] N. Kharasch and M. M. Wald, *Analyt. Chem.*, 1955, **27**, 996.

The reaction of 2,4-*dinitrobenzenesulphenyl bromide with mercurous fluoride.* 2,4-Dinitrobenzenesulphenyl bromide (2 g.) in acetic acid (50 ml.) was shaken at room temperature with mercurous fluoride (5 g.) for 45 min. Hydrogen fluoride was evolved. The mixture was filtered, the pale yellow filtrate reduced in volume, and crystallised to give yellow needles (1·2 g.), m. p. 100—101° (decomp.). The infrared spectrum of this compound was identical with that of 2,4-dinitrobenzenesulphenyl acetate.[14] Similar results were obtained with sodium fluoride. The starting material does not react with acetic acid under these conditions.

Attempted detection of 2,4-*dinitrobenzenesulphenyl iodide.* 2,4-Dinitrobenzenesulphenyl bromide (1 g.) in carbon tetrachloride (30 ml.) was shaken with potassium iodide for 10 min. The orange-red mixture was filtered, diluted with ethylene dichloride (15 ml.), cyclohexene (15 ml.) added, and the solution heated at 50—60° for 30 min. The mixture was extracted with sodium thiosulphate solution, when a precipitate of bis-2,4-dinitrophenyl disulphide (0·11 g., 11%) was formed and was filtered off. The pale yellow filtrate gave only 2-bromocyclohexyl 2,4-dinitrophenyl sulphide (1·08 g., 83%), m. p. and mixed m. p. 120—121°.

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[14] A. J. Havlik and N. Kharasch, *J. Amer. Chem. Soc.*, 1956, **78**, 1207.