Electrophilic Additions to Alkenes. Part III.[1] The Rate Equation for the Reaction of 2,4-Dinitrobenzenesulphenyl Bromide and Cyclohexene in Carbon Tetrachloride Solution

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

Increases of up to 500% in the rate of reaction of 2,4-dinitrobenzenesulphenyl bromide with cyclohexene in carbon tetrachloride solution have been obtained by the addition of 1-substituted 2,4-dinitrobenzenes. The relative catalytic activity of these compounds is 2,4-dinitroanisole > 2-bromocyclohexyl 2,4-dinitrophenyl sulphide (reaction product) > 1-chloro-2,4-dinitrobenzene. The greater increase in rate obtained with added product than with an equivalent excess of sulphenyl bromide provides an explanation for the steady increase in the value of the observed second-order velocity constant as the reaction proceeds. A rate equation is proposed for the reaction, and the mechanism discussed.

In the previous Communication in this Series,[1] we reported that the reaction of 2,4-dinitrobenzenesulphenyl bromide with cyclohexene in carbon tetrachloride solution was essentially homogeneous and polar. The reaction was first-order in cyclohexene, but the order in sulphenyl bromide varied with the initial concentration and was above unity, the initial rate of reaction following the equation:

$$\text{Initial rate} = k_2^{\circ}[\text{B}][\text{ArSBr}] + k_3[\text{B}][\text{ArSBr}]^2 + k_4[\text{B}][\text{ArSBr}]^3$$

where [B] = [cyclohexene]. As reaction progressed the rate decreased more slowly than would have been expected if this equation described the whole reaction, and

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[1] Part II, D. S. Campbell and D. R. Hogg, *J. Chem. Soc.(B)*, 1966, 109.

consequently some other influence remained unidentified. Since the reaction is quantitative and forms only one product, the effect of this product and other compounds of similar structure on the rate of reaction has been investigated to determine the cause of this deviation from the initial rate equation.

RESULTS AND DISCUSSION

The observed initial second-order velocity constants for the reaction of 2,4-dinitrobenzenesulphenyl bromide with cyclohexene in the presence of added dinitro-compounds in carbon tetrachloride solution at 50° are given in Table 1. Observed initial velocity constants are plotted against concentration of added dinitro-compound in the Figure. The line for 2,4-dinitrobenzenesulphenyl bromide, which is based on previously reported data,[1] is added for comparison. In this case the concentration of added dinitro-compound is the amount by which the initial concentration of sulphenyl bromide exceeds 0·039 mole l.$^{-1}$.

TABLE 1

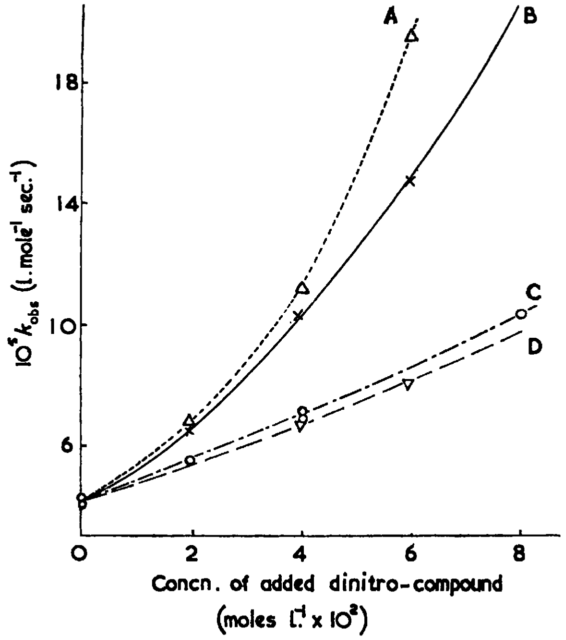
Observed initial velocity constants

$[2,4\text{-}(NO_2)_2\cdot C_6H_3\cdot SBr] = 0{\cdot}039$ mole l.$^{-1}$.
[Cyclohexene] $= 0{\cdot}12$ mole l.$^{-1}$.

Added product (2-*bromocyclohexyl* 2,4-*dinitrophenyl sulphide*)				
Conc. × 10^2 (mole l.$^{-1}$)	—[a]	1·99[b]	3·97	5·96
k_{obs} × 10^5 (l. mole^{-1} sec.$^{-1}$) ...	4·1	6·4	10·3	14·7
Added 2,4-*dinitroanisole*				
Conc. × 10^2 (mole l.$^{-1}$)	1·98	3·97	5·95	
k_{obs} × 10^5 (l. mole^{-1} sec.$^{-1}$) ...	6·7	11·1	19·5	
Added 1-*chloro*-2,4-*dinitrobenzene*				
Conc. × 10^2 (mole l.$^{-1}$)	3·92	5·86		
k_{obs} × 10^5 (l. mole^{-1} sec.$^{-1}$) ...	6·7	8·0		

[a] Previously reported.[1] [b] [Cyclohexene] $= 0{\cdot}10$ mole l.$^{-1}$.

The increase in the observed initial second-order velocity constant with increasing concentration of sulphenyl bromide was attributed[1] to solvation of the transition state by sulphenyl bromide molecules owing to the low solvating power of the solvent, carbon tetrachloride. As all the added compounds in Table 1 have structures similar to that of the sulphenyl bromide and are relatively polar compared with the solvent, their catalytic activity is likely to have a similar origin. The order of catalytic activity, 2,4-dinitroanisole > product (2-bromocyclohexyl 2,4-dinitrophenyl sulphide) > 2,4-dinitrobenzenesulphenyl bromide ⩾ 1-chloro-2,4-dinitrobenzene, is also the expected order of electron release to the nitro-groups from the substituent (-OMe > -SR > -SBr > -Cl). This electron release should be greater in the case of the *p*-nitro-groups as the *o*-nitro-groups would be expected to be twisted out of the plane of the ring.[2] We consider that the catalytic activity of these compounds is due to solvation of the developing positive charge in the transition state leading to the episulphonium-ion intermediate.[3] The *p*-nitro-group is largely responsible for this solvation, which is more efficient the greater the electron density on the oxygen atoms of the group. Nitro-group solvation is not essential for reaction in solvents of low solvating power, as is shown by the appreciable magnitude of the initial second-order velocity constant extrapolated to infinite dilution.[1] Neither is the polarity effect unique to nitro-groups, as the velocity constant for the addition of 2,4-dinitrobenzenesulphenyl chloride to cyclohexene increases rapidly with increasing solvent polarity.[4]



Plot of k_{obs} against concentration of added dinitro-compound; (A), 2,4-dinitroanisole; (B), product; (C), 2,4-dinitrobenzenesulphenyl bromide; (D), 1-chloro-2,4-dinitrobenzene

If the equation for the initial rate of reaction between 2,4-dinitrobenzenesulphenyl bromide and cyclohexene in carbon tetrachloride solution is to be extended to cover the whole reaction, then additional terms will be required to allow for the more efficient solvation by the product than by the sulphenyl bromide. The expression:

$$\begin{aligned}\text{Rate} = k_2^{\circ}[\text{B}][\text{ArSBr}] + k_3[\text{B}][\text{ArSBr}]^2 + \\ k_4[\text{B}][\text{ArSBr}]^3 + k_5[\text{B}][\text{ArSBr}][\text{P}] + \\ k_6[\text{B}][\text{ArSBr}][\text{P}]^2 + k_7[\text{B}][\text{ArSBr}]^2[\text{P}],\end{aligned}$$

where [P] = [Product], allows for solvation of the transition state by one, or by two molecules, which may be either reactant or product. Since k_2°, k_3, and k_4 are known,[1] and the sulphenyl bromide concentration is constant, k_{obs}, the observed initial second-order velocity constant in the presence of added product, will be given by the expression:

$$k_{obs} = K + k_5[\text{P}] + k_6[\text{P}]^2 + k_7[\text{ArSBr}][\text{P}],$$

from which the average values, $k_6 = 1{\cdot}7 \times 10^{-2}$ l.^{3} mole^{-3} sec.$^{-1}$, and $k_5 + k_7$ [ArSBr] $= 0{\cdot}8 \times 10^{-3}$ l.^{2} mole^{-2}

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[2] K. J. Watson, *Nature*, 1960, **188**, 1102.

[3] N. Kharasch and C. M. Buess, *J. Amer. Chem. Soc.*, 1952, **74**, 3422.

[4] D. R. Hogg and N. Kharasch, *J. Amer. Chem. Soc.*, 1956, **78**, 2728.

sec.$^{-1}$, may be obtained. The calculation of values for k_5 and k_7 was not considered justified owing to the magnitude of the experimental error, and the small differences involved in the calculation. To test this rate equation, the rates of reaction at various percentages of reaction were calculated for a reaction 0·0796 mole l.$^{-1}$ in sulphenyl bromide, and 0·0557 mole l.$^{-1}$ in cyclohexene. The values are compared with those obtained from previously recorded data [1] in Table 2. In view of the error involved in obtaining the observed rate by taking tangents, and that introduced by neglecting the variation of $k_5 + k_7$ [ArSBr] with sulphenyl bromide concentration, the agreement is good, and supports the postulated rate expression.

TABLE 2

Comparison of observed and calculated rates of reaction

Percentage completion of reaction	Observed rate × 10^7 (mole l.$^{-1}$ sec.$^{-1}$)	Calculated rate × 10^7 (mole l.$^{-1}$ sec.$^{-1}$)
0	3·01	3·11
20	2·17	2·21
40	1·57	1·52
50	1·27	1·23
60	0·90	0·95
70	0·63	0·68
80	0·45	0·42

The corresponding values to k_6 for 2,4-dinitroanisole and 1-chloro-2,4-dinitrobenzene are $3{\cdot}3 \times 10^{-2}$, and $1{\cdot}0 \times 10^{-3}$ l.$^{-3}$ mole^{-3} sec.$^{-1}$, respectively.

The terms in the proposed rate equation make a clear distinction between the molecularity of several possible transition states. We consider that these transition states must represent limiting cases in a wide range of situations in which the polar entity can modify the solvation shell and facilitate reaction. This rate equation is best explained on the basis of a bimolecular reaction where the kinetics are complicated by the need for solvation, and by the greater solvating power of the product. There seems to be no need to postulate any fundamental change in the reaction mechanism, which is considered to resemble that proposed for the reaction in acetic acid solution.[5]

EXPERIMENTAL

Details of the experimental procedure, and of the reactants and solvent are given in Part II.[1] 2,4-Dinitroanisole, m. p. 89°, prepared by a method similar to that described by Blom,[6] and 1-chloro-2,4-dinitrobenzene, m. p. 52—53°, were recrystallised to constant m. p. before use.

Rates were measured dilatometrically, the reactions being followed to 60% completion. The initial rate constants were obtained by multiplying the initial slope of the plot of meniscus height against time by D/R, the value of R being taken as $2{\cdot}62 \times 10^{-2}$ l. mole^{-1}, the average value for R previously reported [1] for runs with excess cyclohexene.

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[5] D. S. Campbell and D. R. Hogg, *J. Chem. Soc.*, 1965, 5887.

[6] A. V. Blom, *Helv. Chim. Acta*, 1921, **4**, 1029.