

KINETICS OF BROMINE ADDITION TO ACRYLONITRILE AND METHACRYLONITRILE IN AQUEOUS SOLUTION

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ABSTRACT

The kinetics of bromination of acrylonitrile and methacrylonitrile in the presence of bromide ions in aqueous medium were studied by the potentiometric method. The importance of potentiometry over titrimetry is emphasized. The reaction proceeds mainly by Br_3^- species. Values of rate constants and activation energy were evaluated and interpreted in terms of a suitable mechanism.

INTRODUCTION

A number of mechanisms have been proposed for the bromination of alkenes in the presence of bromide ions¹⁻⁴. However, controversy still persists regarding the electrophilic activity of the tribromide species³⁻⁸. The contribution by Br_3^- species is found to be large with deactivated compounds^{1,4,7}. The present work has been undertaken to reinvestigate these mechanisms with the help of kinetic experiments.

MATERIALS AND METHODS

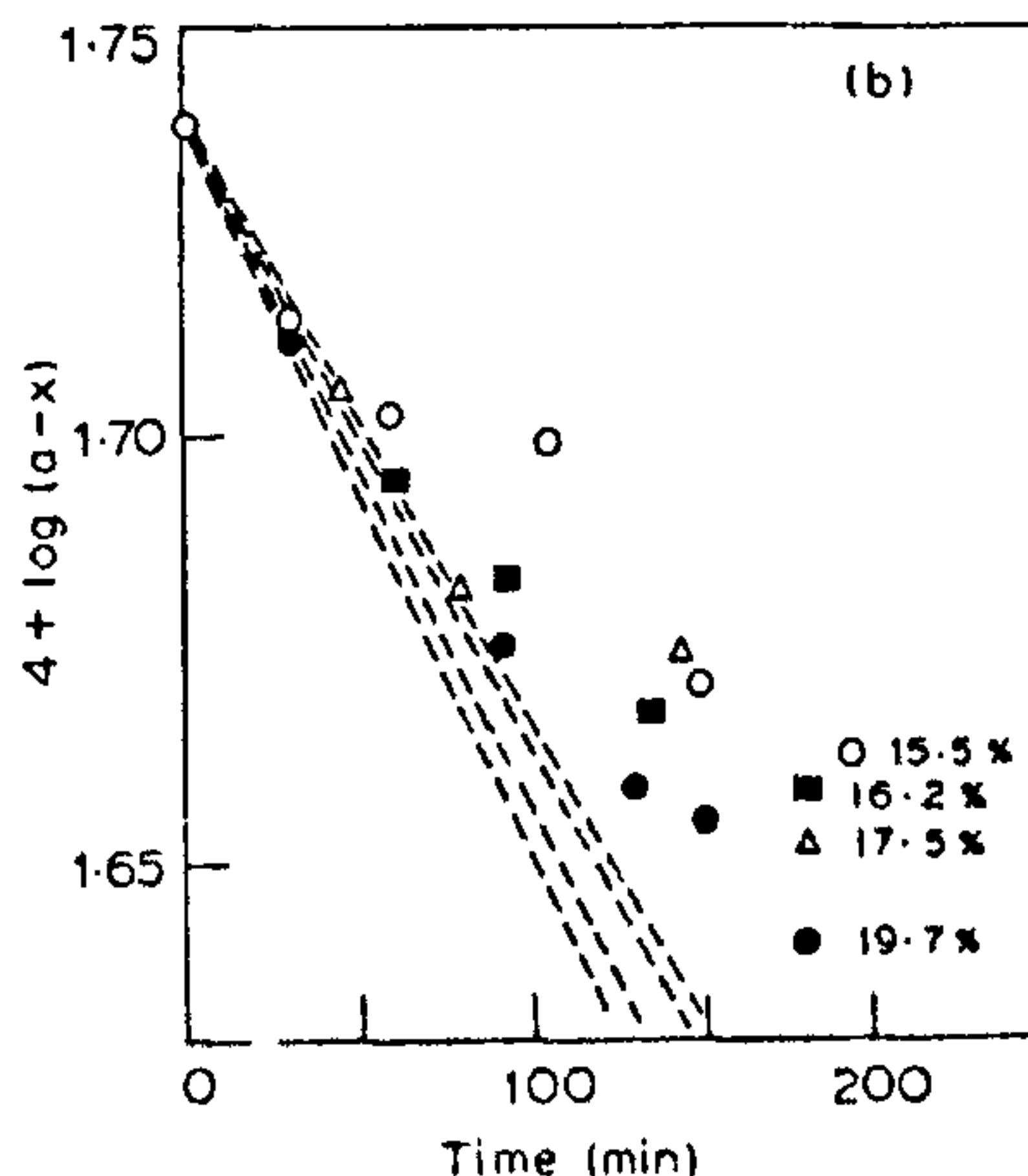
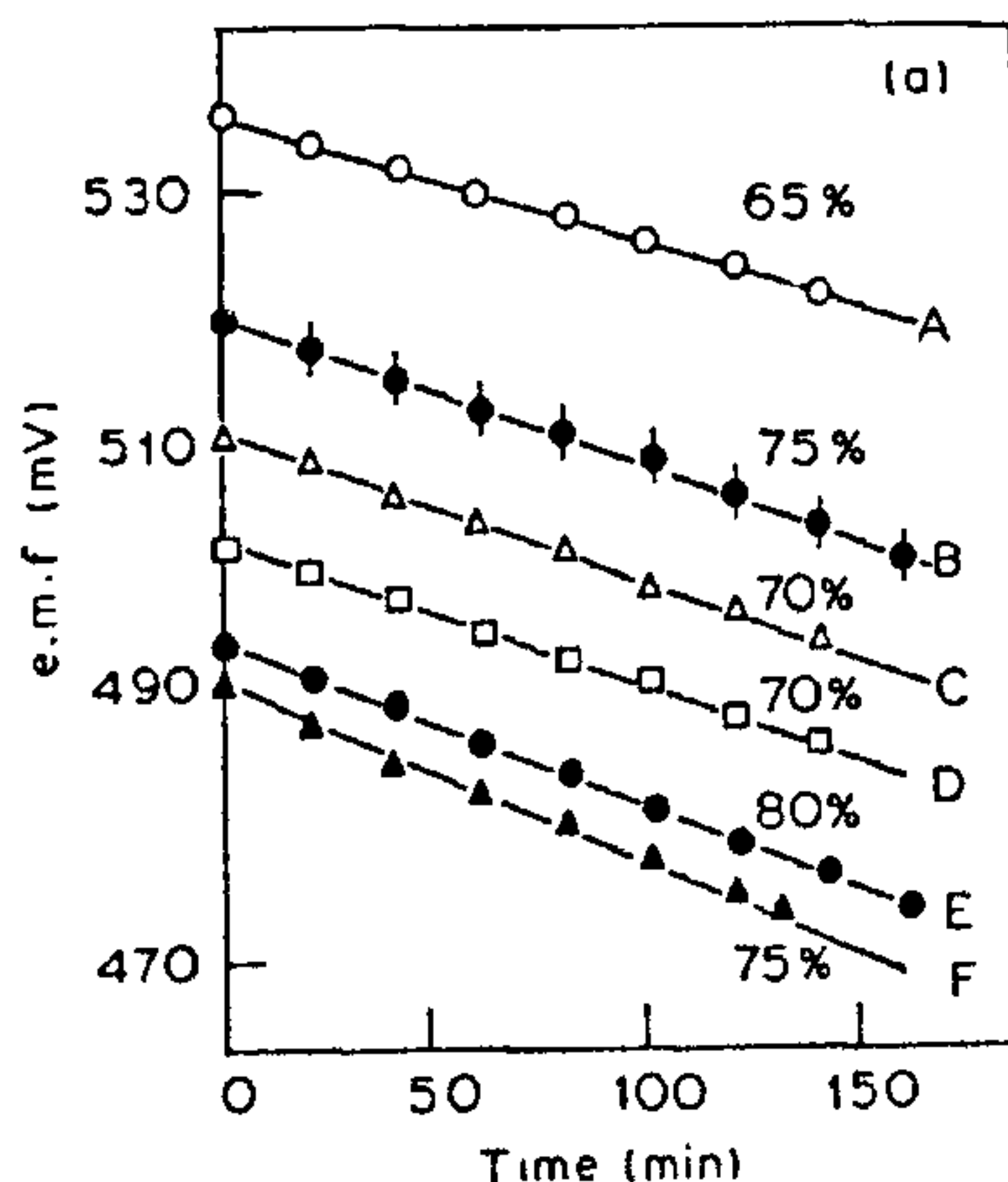
Acrylonitrile (S.D.'s Lab. Reagent) and methacrylonitrile (American Cyanamide Company) were

purified by first washing with alkali (5% aqueous solution) to remove the inhibitor and then with 3% phosphoric acid to remove any basic impurities. The compounds were then washed with water and then dried over anhydrous calcium chloride. They were distilled in an atmosphere of nitrogen under reduced pressure, repeatedly and stored at 278 K.

Sodium bromide (LR Sarabai Chemicals) was purified by recrystallization⁹. Perchloric acid (GR) and bromine (GR) were used as such.

Kinetic procedure

All the kinetic experiments were carried out by the potentiometric method using Pt, Br_2/Br^- and glass



Figures 1a,b. Comparison of potentiometric and titrimetric methods for acrylonitrile-bromine reaction in water at 303 K. a. Potentiometry $-\text{[Br}^-]$ (mol dm^{-3}): A, 0.10; B, 0.15; C, 0.20; D, 0.25; E, 0.30; F, 0.35. b. Titrimetry $-\text{[Br}^-]$ (mol dm^{-3}): O, 0.1; Δ , 0.2; \bullet , 0.3; \blacksquare , 0.4.

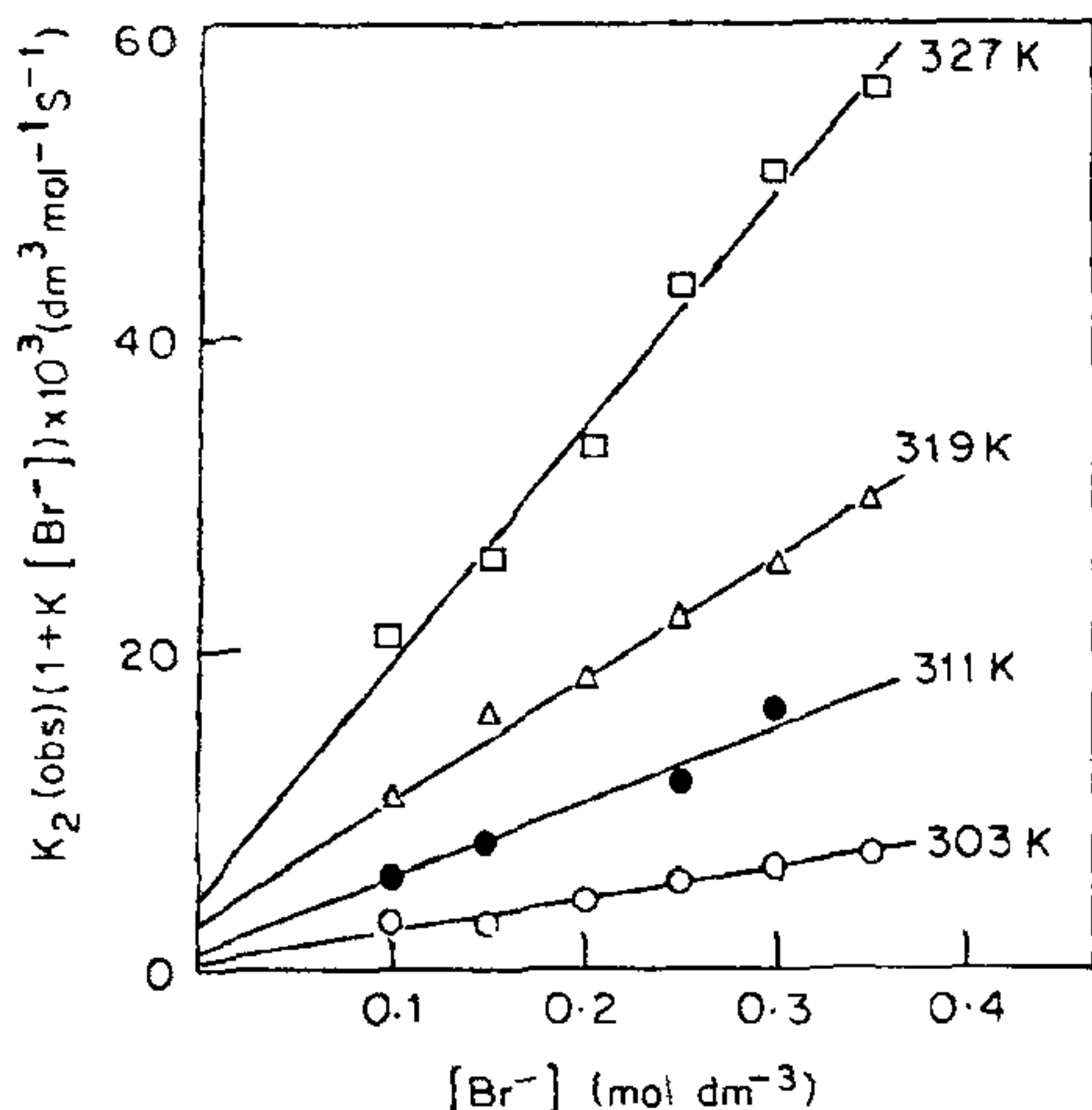


Figure 2. Determination of k_{Br_2} and $k_{Br_3^-}$ at different temperatures for acrylonitrile-bromine reaction in water.

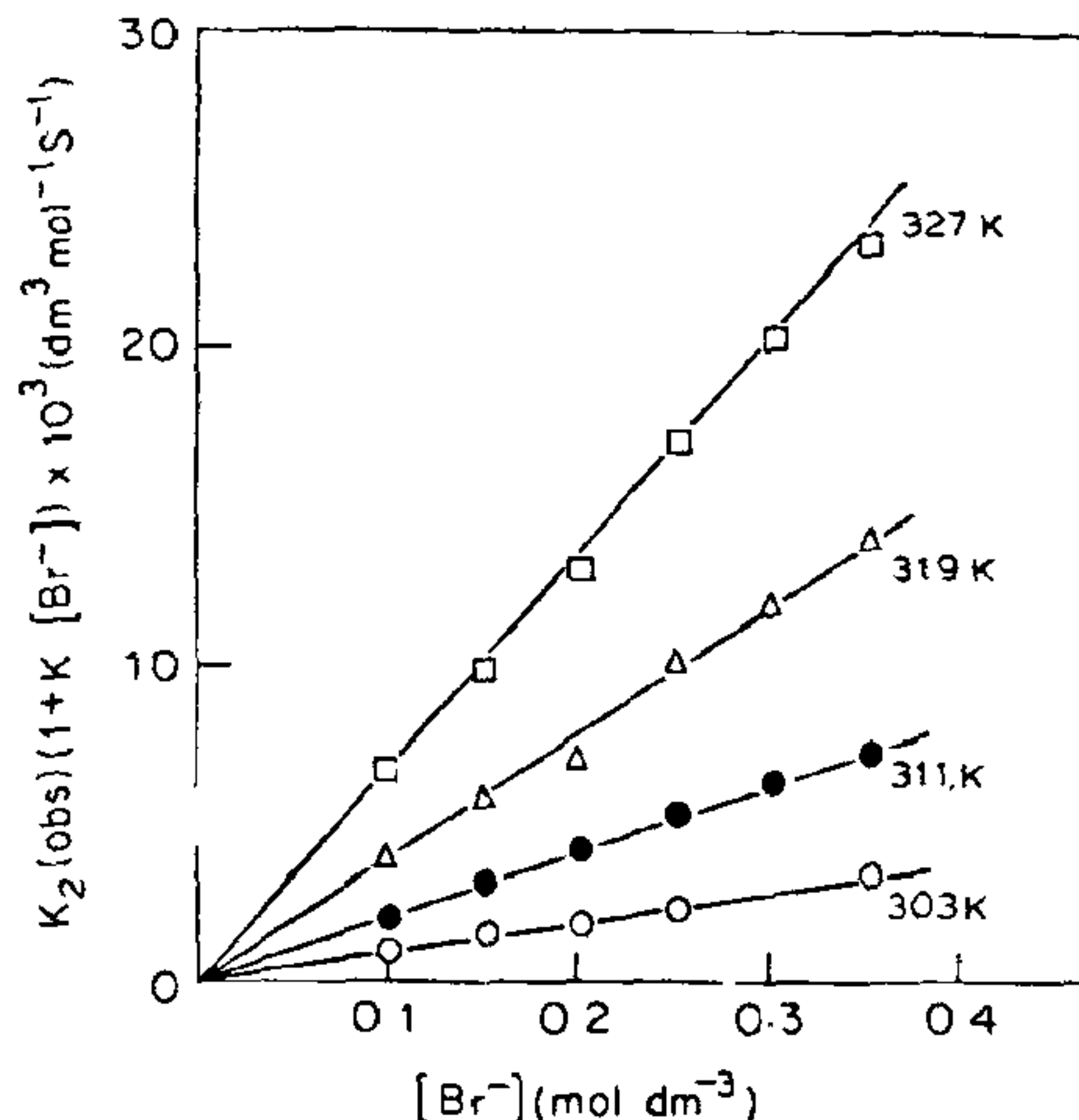


Figure 3. Determination of k_{Br_2} and $k_{Br_3^-}$ at different temperatures for methacrylonitrile-bromine reaction in water.

electrodes fitted into a specially fabricated reaction vessel⁹.

The concentration of the substrate used ranged from 0.08 to 0.3 mol dm⁻³ and the initial bromine concentration from 10⁻² to 10⁻³ mol dm⁻³. The bromide concentration was varied by 40 times i.e. from 0.01 to 0.4 mol dm⁻³. In all the experiments the concentration of HClO₄ used was maintained at 0.1 mol dm⁻³. The reactions were conducted at 303, 311, 319 and 327 K. At each temperature, kinetic runs were carried out at different bromide concentrations.

In each reaction, the emf falls linearly with time (figure 1a) showing first order in bromine. The pseudo-first order rate constants (k_1) were obtained from the slope of the plots³ of E vs time. The second order rate constants, $k_2(\text{obs})$, were obtained by dividing k_1 by initial concentration of substrate.

The second order specific reaction rate, $k_2(\text{obs})$, is a composite factor of k_{Br_2} and $k_{Br_3^-}$ corresponding to the reactions by Br_2 and Br_3^- species, respectively and can be expressed¹⁰ as

$$k_2(\text{obs}) = k_{Br_2} + k_{Br_3^-} K [Br^-] / (1 + K [Br^-]).$$

By employing the least square method for the K values of Scaife and Tyrrell¹¹, the values at other required temperatures have been evaluated. k_{Br_2}

and $k_{Br_3^-}$ were obtained from the plots of $k_2(\text{obs})(1 + K[Br^-])$ against $[Br^-]$ (figures 2 and 3).

RESULTS AND DISCUSSION

The powerful deactivating influence ($-I$, $-T$) of cyanide group in nitriles on electrophilic reactivity is revealed in the slow rate even in polar solvents like water.

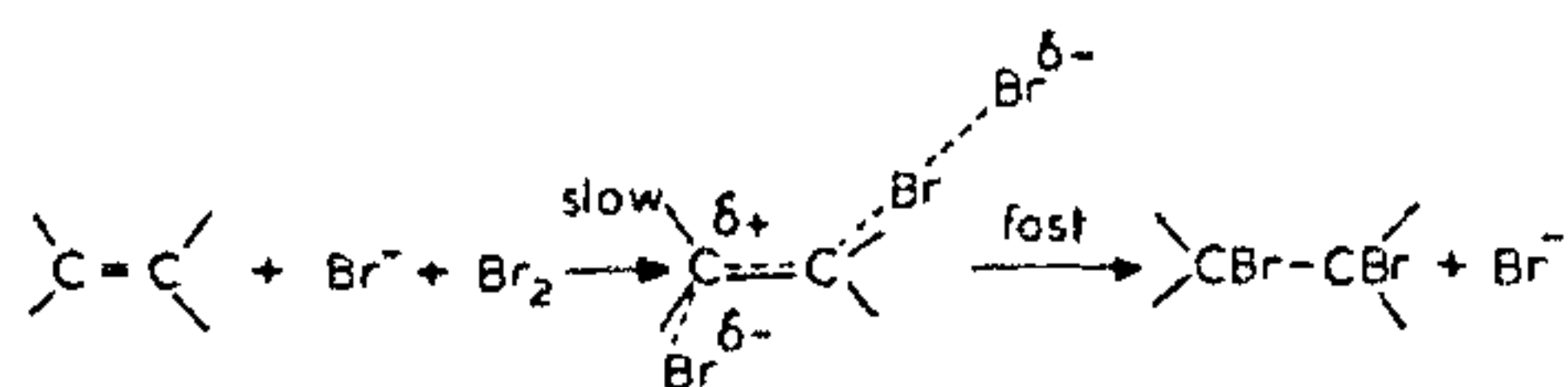
Attempts were first made to follow the kinetics by titrimetry. It was found that the reaction rates were highly irregular and not reproducible (figure 1b). But when the kinetic study was made by potentiometry the reaction not only proceeded very smoothly but very good straight line graphs were also obtained for "emf vs time" (figure 1a). A comparison of titrimetric and potentiometric studies (figure 1) clearly shows that such an erratic behaviour and apparent slowness of the reaction in the titrimetry may not be due to polymerization as attributed by Evans *et al*¹² in their study on bromination of crotono- and acrylo-nitriles in acetic acid medium at 298 K, but is actually due to the debromination of the product, a dibromo compound, in the presence of iodide as a result of which there is extra-iodine liberation besides that liberated by unreacted bromine. There was thus an increase in the titre value amounting to an apparent fall in

reaction rate as the reaction proceeded. Thus potentiometry forms the most versatile method for studying the kinetics of bromination of compounds such as nitriles whose dibromides undergo debromination by iodide ions.

In figure 2 the zero intercept shows negligible contribution by Br_2 species for acrylonitrile-bromine reaction. For methacrylonitrile, however, the contribution by Br_2 species to the reaction rate has been significant, though small, compared to that by Br_3^- species (figure 3). In the bromination kinetics of nitriles, $k_2(\text{obs})$ was found to vary linearly with bromide-concentration and the contribution by $k_{\text{Br}_3^-}$ for nitriles was greater than k_{Br_2} . Such an increase in $k_{\text{Br}_3^-}$ compared to k_{Br_2} has also been observed with other deactivated compounds such as diethyl fumarate^{3,4}, diethylmaleate⁴ and 3-nitro- and 4-nitro-styrenes⁷. This type of trend in $k_{\text{Br}_3^-}/k_{\text{Br}_2}$ observed mostly in deactivated substrates is due to the increased contribution of nucleophilic assistance by Br^- .

The activation energies of nitriles were calculated by Arrhenius plots using $k_{\text{Br}_3^-}$ values. The higher activation energies, E_a , of these compounds compared with those of the derivatives of acrylic and methacrylic acids⁹ signify that the electron density at the reaction site is depleted much by the powerful electron-withdrawing $-\text{CN}$ group and the specific reaction rate has come down to about $10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ (table 1). E_a for methacrylonitrile with extra methyl group is less than that of acrylonitrile. The magnitude of decrease in E_a is very small (1.3 kJ mol^{-1}). Thus the rate increase is only 2 times instead of about 30 times as in other pairs of compounds, for example, acrylamide and methacrylamide⁹, due to the highly deactivating $-\text{CN}$ group in the presence of which the effect due to the methyl group has not been fully felt by the alkenic carbon atoms.

In spite of Br_3^- being less reactive as an electrophile than Br_2 , the observed greater value for $k_{\text{Br}_3^-}$ than k_{Br_2} , indicates the predominant assistance by Br^- to the reaction, and the mechanisms may be given as follows:



Though $k_{\text{Br}_3^-}$ is a composite term^{5,8,13,14}, in highly deactivated substrates like acrylonitrile and methac-

Table 1 Rate constants, $k_2(\text{obs}) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ at different $[\text{Br}^-]$'s and temperatures for AN, MAN-bromine reaction in water

$[\text{Br}^-]$ (mol dm^{-3})	303(K)	311(K)	319(K)	327(K)
AN				
0.10	3.81	7.72	15.75	29.24
0.15	4.23	9.43	18.52	33.10
0.20	4.38	10.58	18.61	36.02
0.25	4.42	11.39	22.33	39.53
0.30	4.96	11.80	22.61	41.01
0.35	5.18	11.73	23.26	42.23
MAN				
0.10	12.49	23.82	44.16	90.96
0.15	9.84	24.57	51.22	88.36
0.20	11.18	—	47.90	92.78
0.25	11.59	25.16	48.96	100.85
0.30	11.78	30.29	48.75	101.49
0.35	11.31	—	49.95	99.76

Table 2 Rate constants, K_{Br_2} and $K_{\text{Br}_3^-}$ at different temperatures for AN, MAN - bromine reaction in aqueous medium

Temperature (K)	AN		MAN
	$K_{\text{Br}_3^-} \times 10^3$ ($\text{dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$)	$K_{\text{Br}_2} \times 10^3$ ($\text{dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$)	$K_{\text{Br}_3^-} \times 10^3$ ($\text{dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$)
303	0.58	0.7	1.21
311	1.42	1.3	3.17
319	2.82	3.2	5.23
327	5.23	5.5	11.10

rylonitrile, the termolecular reaction Br^- -catalyzed Br_2 species addition, in which the attack by Br^- is a slow step leading to dibromide, predominates.

ACKNOWLEDGEMENT

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NEWS

NEW MATERIAL FOR COMBATING OIL-SPILLS

The material developed by Leningrad experts absorbs like a sponge oil products from the water surface. Experiments carried out at the Institute of Peat Industry showed that thermal treatment of peat makes it very light-weight and porous. Twelve-metre sections made of it and used for enclosing the polluted area weigh only 12 kilos. The weight of the oil they absorb exceeds their own weight by many times.

The material named "bertinat" can be used for combating oil spills. In Leningrad there is a fleet of

150 vessels fitted out with equipment for clearing the water surface, lifting the sunk timber and cutting seaweeds. There are "ecological" vessels at the disposal of many major enterprises with specified water area. Over a navigation season, more than 6,000 cargo ships pass through the Neva river, linking the largest European Lake Ladoga and the Gulf of Finland. (*Soviet Features*, Vol. XXV, No. 172, p. 5., 1986; Information Department, USSR Embassy in India, 25 Barakhamba Road, New Delhi 110 001).