

# Comparative Study of Kinetics of Oxidation of Aliphatic Primary Amines by *N*-Bromosuccinimide in Acidic and Basic Solutions

P. SAROJA\* and SUSHAMA KANDLIKAR

Department of Chemistry, S. N. V. M. V. College, Hyderabad-500 001

Manuscript received 12 May 1989, revised 3 April 1990, accepted 24 September 1990

The title reaction studied in the presence of mercuric acetate and sulphuric acid is first order each in [NBS] and amine. Increase in  $[H^+]$  increased the rate marginally. The rate of reaction increased with decrease in dielectric constant of the medium. The observed order of reactivity of different amines towards oxidation was: methyl < ethyl < *n*-propyl < *n*-butyl isobutyl < isopropyl amine. The oxidation of these amines by NBS in basic solution was also first order each in [NBS] and [amine]. Increase in  $[OH^-]$  increased the rate of reaction while added succinimide decreased the rate of oxidation. The rate of reaction decreased with decrease in dielectric constant of the medium. The order of reactivity of different amines towards oxidation was found to be just the reverse of that observed in acid solution. Applicability of Taft's equation was tested in both the reactions. The rate constants ( $k'$ ) and activation parameters have been evaluated and suitable mechanisms in conformity with the experimental observations have been suggested.

*N*-Bromosuccinimide (NBS) has been extensively used as an oxidising agent and analytical reagent<sup>1</sup>. Though there are a large number of reports on the kinetics and mechanism of oxidation of organic/inorganic compounds by NBS<sup>2</sup> in acid solution, there is no report in literature on similar studies of oxidation of any substrate in basic solution. Recently, we have proposed and reported a mechanism involving the hypobromite ion as the active oxidising species of NBS in basic solution in the oxidation of oxalate ion on the basis of salt and solvent effects and product analysis<sup>3</sup>. There is no report in literature on the kinetics of oxidation of aliphatic primary amines by NBS in acid solution which prompted the authors to undertake a comparative study of kinetics of this oxidation in acidic and basic solutions with a view to find out the differences in mechanism.

## Experimental

All the amines (Fluka) were distilled before use. NBS (G. R., S. Merck) was used. Acetic acid was purified by the literature procedure<sup>4</sup>. The products of oxidation were identified as the corresponding aldehydes by the m.ps. of their 2,4-DNP derivatives. The course of the reaction was followed by estimating the unreacted NBS iodometrically<sup>1</sup> under pseudo-first order conditions, i.e.  $[NBS] \ll [amine]$ . The second order rate constants were calculated using the equation,  $k'' = k'_{pseudo}/[amine]$ . All rate constants reported are reproducible within 3–5% error.

## Results and Discussion

**Oxidation in acid solution:** Under the experimental conditions  $[NBS] \ll [S]$  (*S*—substrate), the

order in [NBS] was unity as obtained from a linear plot of  $\log(a-x)$  vs time (Table 1). The order in [ethyl amine] as obtained from the plot of  $\log k'$  vs  $\log [S]$  was one (Table 2). The rate of reaction showed a marginal increase with increase in  $[H^+]$  over a wide range of  $[H^+]$  employed (Table 2) and the order in  $[H^+]$  was obtained as 0.3. A four-fold change in mercuric acetate (acting as a bromine scavenger) from 0.02–0.08 mol dm<sup>-3</sup> had a negligible effect on the rate of oxidation. Added succinimide in the range 0.02–0.1 mol dm<sup>-3</sup> had a negligible retarding effect on rate. Addition of salts, viz. NaClO<sub>4</sub> etc. in the concentration range 0.05–0.5 mol dm<sup>-3</sup> did not have much effect on the rate of reaction. The rate of reaction increased with an increase in the percentage of acetic acid in the solvent medium. A plot of  $\log k'$  vs  $1/D$  was

TABLE 1—ORDER IN [NBS] IN NBS-ETHYLAMINE REACTION IN ACID SOLUTION

$[NBS] = 5.00 \times 10^{-3}$  mol dm<sup>-3</sup>, [ethylamine] =  $5.00 \times 10^{-3}$  mol dm<sup>-3</sup>,  $[H_2SO_4] = 5.00 \times 10^{-2}$  mol dm<sup>-3</sup>,  $[Hg(OAc)_2] = 2.00 \times 10^{-2}$  mol dm<sup>-3</sup>, Temp. = 303 K

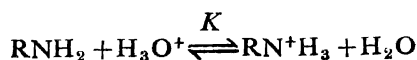
Time (t) min	Titre value (a-x)/5 ml	log (a-x)
0	19.0	1.279
10	17.8	1.250
20	16.6	1.220
30	15.6	1.193
40	14.7	1.167
50	13.4	1.127
60	12.6	1.100
70	11.8	1.072
80	11.00	1.041
90	10.3	1.013
100	9.6	0.982
110	8.9	0.949
120	8.3	0.919

TABLE 2—ORDER IN [ETHYLAMINE] AND [H<sub>2</sub>SO<sub>4</sub>] IN ETHYLAMINE-NBS REACTION IN ACID SOLUTION[NBS] = 5.00 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [Hg(OAc)<sub>2</sub>] = 2.00 × 10<sup>-2</sup> mol dm<sup>-3</sup>, Temp. = 303 K

[Ethylamine] × 10 <sup>2</sup> mol dm <sup>-3</sup>	[H <sub>2</sub> SO <sub>4</sub> ] × 10 <sup>2</sup> mol dm <sup>-3</sup>	k' × 10 <sup>4</sup> s <sup>-1</sup>
5.00	5.00	1.67
10.0	5.00	3.30
20.0	5.00	6.61
30.0	5.00	10.0
40.0	5.00	13.0
5.00	5.00	1.66
5.00	10.0	1.89
5.00	20.0	2.11
5.00	40.0	2.37
5.00	80.0	2.67
5.00	160	3.00
5.00	200	3.33

linear with a positive slope. No polymerisation was observed when the reaction was carried out in the presence of acrylamide monomer indicating that a free-radical mechanism was not operative. Stoichiometric studies revealed that one mole of amine consumed one mole of NBS to give one mole of carbonyl compound and ammonia.

Amines are converted into their salts by mineral acids,



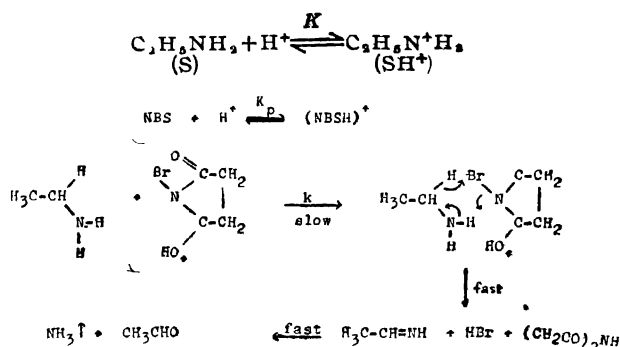
Their approximate  $K_b$  values are in the range of 10<sup>-4</sup>.

NBS is also known to be protonated in acid solution as



In the present study it was observed that the rate increased marginally with increase in [H<sup>+</sup>] over a wide range of [H<sup>+</sup>] employed in the reaction. This may be explained by assuming a reaction between the protonated NBS and unprotonated amine in the rate-determining step resulting in a compensatory effect of [H<sup>+</sup>] on rate. The opposite, i.e. the unprotonated NBS and protonated amine as the active species is not probable since in any oxidation the flow of electrons must be towards the oxidant. The probability of Br<sup>+</sup>, H<sub>2</sub>OBr<sup>+</sup> or HOBr as the oxidising species was ruled out as the addition of succinimide did not result in any inhibition of rate of reaction. Mercuric acetate oxidation of amine was also ruled out based on the zero effect of added mercuric acetate on the rate of oxidation.

From the above results the following mechanism involving the formation of a cyclic transition state in the rate-controlling step is proposed (Scheme 1).



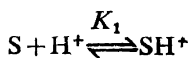
Scheme 1

Scheme 1 leads to rate law (1),

$$-d[\text{NBS}]/dt = k[(\text{NBSH})^+][\text{S}], \quad (f = \text{free}) \quad (1)$$

$$K_p = [(\text{NBSH})^+]/[\text{NBS}]_t [\text{H}^+]$$

$$[(\text{NBSH})^+] = [\text{NBS}]_t K_p [\text{H}^+] / \{1 + K_p [\text{H}^+]\}$$



$$K_1 = [\text{SH}^+] / [\text{S}]_t [\text{H}^+]$$

$$[\text{S}]_t = [\text{S}] / \{1 + K_1 [\text{H}^+]\}$$

On substituting for  $[(\text{NBSH})^+]$  and  $[\text{S}]_t$  the rate law (1) assumes the form,

$$-d[\text{NBS}]/dt = k[\text{NBS}]_t K_p [\text{H}^+] [\text{S}]_t / (1 + K_p [\text{H}^+]) (1 + K_1 [\text{H}^+])$$

As the  $K_1$  values of amines are in the range of 10<sup>-4</sup>,  $K_1 [\text{H}^+]$  may be neglected in comparison to (1) and the rate law becomes

$$-d[\text{NBS}]/dt = k K_p [\text{NBS}]_t [\text{H}^+] [\text{S}]_t / (1 + K_p [\text{H}^+])$$

which explains the fractional order dependence in [H<sup>+</sup>],

or

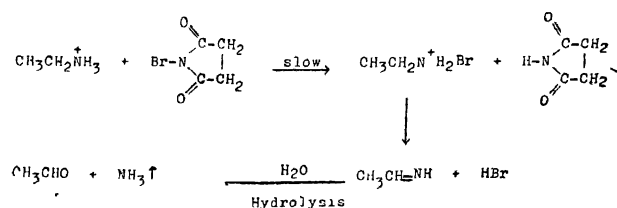
$$-d[\text{NBS}]/dt / [\text{NBS}]_t = k' = k K_p [\text{H}^+] [\text{S}]_t$$

or

$$1/k' = 1/[\text{S}]_t (1 + K_p [\text{H}^+]) / k K_p [\text{H}^+]$$

When  $1/k'$  was plotted against  $1/[\text{S}]_t$ , a straight line was obtained passing through the origin confirming the derived rate law.

An alternative mechanism consisting of protonated amine and unprotonated NBS is shown in Scheme 2.



Scheme 2

Scheme 2 leads to rate law (2),

$$-d[\text{NBS}]/dt = k[\text{NBS}]_t[\text{SH}^+] \quad (2)$$

$$[\text{NBS}]_t = [\text{NBS}]_0 / (1 + K_p[\text{H}^+])$$

$$[\text{SH}^+] = [\text{S}]_0 K_1 [\text{H}^+] / (1 + K_1 [\text{H}^+])$$

On substituting for  $[\text{NBS}]_t$  and  $[\text{SH}^+]$  in rate law (2) we get,

$$-d[\text{NBS}]/dt =$$

$$k[\text{NBS}]_0 [\text{S}]_0 K_1 [\text{H}^+] / ((1 + K_p[\text{H}^+])(1 + K_1 [\text{H}^+]))$$

As the  $K_1$  values of amines are in the range of  $10^{-4}$ ,  $K_1[\text{H}^+]$  may be neglected in comparison to (1) and then we get,

$$-d[\text{NBS}]/dt = k[\text{NBS}]_0 [\text{S}]_0 K_1 [\text{H}^+] / (1 + K_p[\text{H}^+])$$

This rate law is also in agreement with the observed kinetic results. However, since a protonated substrate can not be a good reductant as has already been discussed earlier, mechanism 1 appears to be more probable.

In order to confirm the nature of the reactive species of oxidant and substrate, the solvent effect was studied with the variation of acetic acid content in the aquo-acetic acid mixture. The rate of oxidation increased with increase in the acetic acid content, i.e. with decrease in the dielectric constant of the medium. The plot of  $\log k'$  vs  $1/D$  was linear with a positive slope suggesting a reaction between a positive ion and a dipole in the rate-determining step<sup>6</sup>.

The reactivity of different amines in oxidation was found to increase in the order of the  $+I$  effect of the alkyl group attached to nitrogen, viz. methylamine < ethylamine < n-propylamine < n-butylamine < isobutylamine < isopropylamine. This indicates that the transition state may possess a small amount of carbonium ion character. This may be explained by assuming that the abstraction of hydride ion from  $\alpha$ -carbon by  $(\text{NBSH})^+$  takes place just before the departure of proton from nitrogen,

and in the transition state C-H has undergone more cleavage than N-H since  $(\text{NBSH})^+$  being positively charged, is a stronger electrophile than a neutral molecule (NBS). An attempt has also been made to apply the Taft's equation using the  $\sigma^*$  (Taft' polar substituent constants) values for alkyl substituents<sup>7</sup> (Fig. 1a). When the  $\sigma^*$  values were plotted against  $\log k''/k'_0$  a straight line was obtained with a negative slope ( $\rho^* = -2.7$ ) suggesting that the reaction was susceptible to polar effects and that the

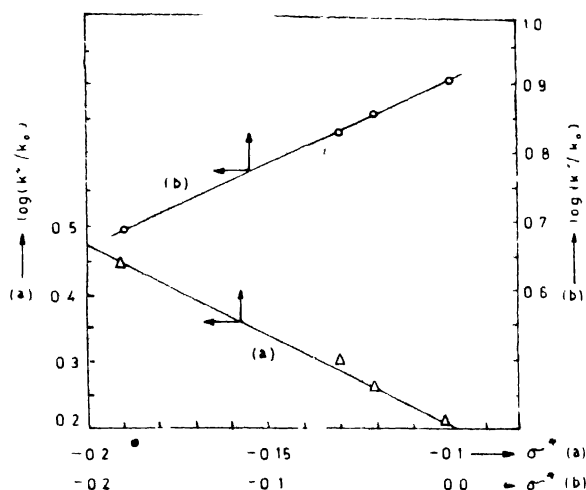


Fig. 1. Taft's plots of  $\log(k''/k'_0)$  vs  $\sigma^*$  in NBS-amine reaction in (a) acid solution, (b) basic solution.

activated complex has a positive ion character. The reaction was carried out at five different temperatures and the activation parameters are calculated (Table 3). The highly negative values of entropy of activation provide support to the proposed cyclic transition state in the mechanism.

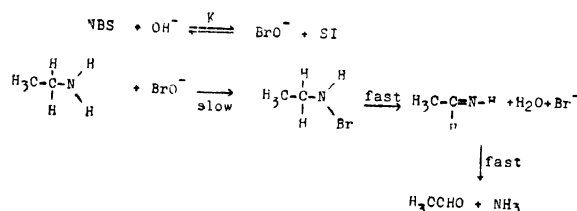
**Oxidation in basic solution:** Under the experimental conditions  $[\text{NBS}] \ll [\text{S}]$ , the order in  $[\text{NBS}]$

TABLE 3—ACTIVATION PARAMETERS OF NBS-AMINE REACTION

$[\text{NBS}] = 5.00 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{Hg}(\text{OAc})_2] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{H}_2\text{SO}_4] = 5.00 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{NaOH}] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$ , Temp. = 303 K

Parameter/ Medium	Methyl amine	Ethyl amine	n-Propyl amine	Iso-propyl amine	n-Butyl amine	Iso-butyl amine
$k'' (\times 10 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$						
A.S.	2.00	3.32	3.66	5.66	4.00	5.00
B.S.	3.66	3.02	2.68	1.84	2.28	2.00
$E_a (\text{KJ mol}^{-1})$						
A.S.	57.4	53.6	49.8	42.1	47.9	44.0
B.S.	53.6	57.4	61.3	70.8	65.1	67.0
$\Delta H^\ddagger (\text{KJ mol}^{-1})$						
A.S.	54.9	51.1	47.3	39.6	45.4	41.5
B.S.	51.1	55.0	58.8	68.3	62.6	64.5
$\Delta G^\ddagger (\text{KJ mol}^{-1})$						
A.S.	89.9	88.6	88.4	87.3	88.1	87.6
B.S.	88.6	88.9	89.2	90.1	89.6	89.9
$-\Delta S^\ddagger (\text{JK}^{-1} \text{ mol}^{-1})$						
A.S.	116	124	136	157	141	152
B.S.	124	112	100	72.0	89.1	83.8

was found to be unity as obtained from a plot of  $\log(ir)$  vs  $\log [NBS]$  which was linear with unit slope (Table 4) ( $ir$ =initial rate). The rate increased with increase in  $[S]$ . The plot of  $\log(ir)$  vs  $\log[S]$  was linear with unit slope indicating first order dependence in  $[S]$  (Table 4). The rate of reaction increased with increase in  $[OH^-]$  and the order in



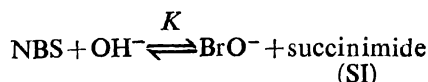
Scheme 3

TABLE 4—ORDER IN [NBS], [ETHYL AMINE] AND [NaOH] IN NBS-ETHYLAMINE REACTION IN BASIC SOLUTION AT 303 K

[NBS] $\times 10^3$ mol dm <sup>-3</sup>	[Ethyl amine] $\times 10^2$ mol dm <sup>-3</sup>	[NaOH] $\times 10^3$ mol dm <sup>-3</sup>	(ir) $\times 10^6$ mol dm <sup>-3</sup> s <sup>-1</sup>
5.00	5.00	1.00	0.750
7.50	5.00	1.00	1.14
10.0	5.00	1.00	1.50
12.0	5.00	1.00	1.80
15.0	5.00	1.00	2.25
5.00	5.00	1.00	0.750
5.00	10.0	1.00	1.55
5.00	20.0	1.00	2.92
5.00	30.0	1.00	4.74
5.00	40.0	1.00	6.05
5.00	5.00	1.00	0.750
5.00	5.00	8.00	2.00
5.00	5.00	16.0	2.80
5.00	5.00	32.0	4.00
5.00	5.00	64.0	5.20

$[OH^-]$  was fractional, viz. 0.5 as obtained from a plot of  $\log(\text{rate})$  vs  $\log [OH^-]$  in the case of ethylamine-NBS reaction (Table 4). Addition of one of the products, succinimide had a retarding effect on the rate of reaction. Hence, in all the reactions in basic solution order was determined by the Vant Hoff's differential rate method. Addition of salts like  $NaClO_4$  had a negligible effect on rate of reaction. The rate of reaction decreased with increase in the proportion of *t*-butyl alcohol, i.e. decrease in dielectric constant of the medium. No induced polymerisation was observed when acrylamide was added to the reaction mixture indicating that a polar mechanism is operating. Stoichiometric studies revealed that one mole of NBS consumed one mole of amine to produce the corresponding carbonyl compound and ammonia.

The increase in rate with increase in  $[OH^-]$  and the retarding effect of added succinimide on rate of oxidation suggest the following pre-equilibrium step prior to the rate-controlling step involving succinimide as one of the products,



The observed first order dependence in  $[NBS]$  as well as in  $[S]$  is suggestive of a mechanism shown in Scheme 3 taking ethylamine as a typical example. This Scheme envisages a bimolecular nucleophilic substitution as the rate-controlling step, followed by an abstraction of an  $\alpha$ -proton by the hydroxide ion and simultaneous elimination of bromide ion,

resulting in the formation of an imine which undergoes rapid hydrolysis to give the carbonyl compound and ammonia.

Scheme 3 leads to rate law (3),

$$-d[NBS]/dt = k[S][BrO^-] \quad (3)$$

$[BrO^-]$  is derived as follows :

$$K = [BrO^-][SI]/[NBS]_t[OH^-]_t - [SI] \quad (f = \text{free})$$

$$[BrO^-] = K[NBS]_t([OH^-]_t - [SI])/[SI]$$

$[NBS]_t$  is derived as follows :

$$[NBS]_t = [NBS] + [BrO^-]$$

$$[NBS]_t = [NBS]_i \{1 + K([OH^-]_t - [SI])/[SI]\}$$

$$[NBS]_t = [NBS]_i [SI] / \{[SI] + \{K([OH^-]_t - [SI])\}\}$$

On substituting for  $[BrO^-]$  in rate law (3) we get,

$$-d[NBS]dt = kK[S][NBS]_i \{[OH^-]_t - [SI]\} / \{[SI] + K\{[OH^-]_t - [SI]\}\}$$

or

$$-d[NBS]/dt/[NBS] = k' = kK[S]\{[OH^-]_t - [SI]\} / \{[SI] + K\{[OH^-]_t - [SI]\}\}$$

or

$$1/k' = [SI]/Kk\{[OH^-]_t - [SI]\}[S] + 1/k[S]$$

The plot of  $1/k'$  vs  $1/[S]$  was linear passing through the origin confirming the derived rate law. This equation explains all the experimental observations.

The decrease in rate with decrease in the dielectric constant of the medium also supports the proposed negative ion-dipole reaction in the rate-determining step and indicates that the activated complex is more polar than the reactants. The order of reactivities of different amines towards oxidation was observed to be : methylamine > ethylamine > *n*-propylamine > *n*-butylamine > isobutylamine > isopropylamine, indicating that the activated complex has a negative ion character. Taft's equation was found to be applicable and when  $\log k''/k''_0$  was plotted against  $\sigma^*$ , a straight line was obtained with a positive slope ( $\rho^* = 2.5$ ) indicating that the activated complex is negatively charged (Fig. 1b). This may be explained by assuming that the abstraction of  $\alpha$ -proton by the hydroxide ion occurs prior to the elimination of bromide ion, thus imparting some carbanion character to the activated complex. The reactions were carried out at five different temperatures and the activation parameters calculated (Table 3). The

$\Delta S^\ddagger$  values are highly negative indicating crowding in the transition state. When two molecules come together to form a single activated complex the entropy increases considerably. The activation enthalpies and entropies of the oxidation are linearly related in both the cases of acidic and basic solutions. The correlation was tested and found genuine by applying Exner's criterion<sup>8</sup>. The isokinetic temperature computed from the plot of  $\log k'_{303}$  vs  $\log k'_{308}$  ( $r=0.99$ ) was found to be 333 K in acid solution and 340 K in basic solution. As the amines studied were low-boiling, attempts to find out if the order of reactivity was reversed above the isokinetic temperature were not successful.

A comparison of the oxidation of aliphatic amines in acidic and basic solutions reveals that though the products obtained were the same, the order of reactivity, the nature of transition state and the mechanisms were totally different. The oxidation in acid solution may be proceeding via a hydride ion abstraction by (NBSH)<sup>+</sup> as proposed while a proton can be easily eliminated by the hydroxide ion in basic solution. The reverse order of reactivities and the sign of  $\rho^\ddagger$  lends support to the different mechanisms proposed in acidic and basic solutions.

#### Acknowledgement

The authors are thankful to Prof. T. Nayneeth Rao, Vice-Chancellor of Osmania University and to Prof. B. Sethuram for helpful discussions. One

of the authors (P. S.) is thankful to the Principal of S.N.V.M.V. College, Dr. (Mrs.) Sulochana Mathur for facilities.

#### References

1. N. K. MATHUR and C. K. NARANG, "The Determination of Organic Compounds with *N*-Bromosuccinimide and Allied Reagents", Academic, New York, 1975.
2. N. VENKATSUBRAMANIAN and V. THIAGARAJAN, *Can. J. Chem.*, 1969, **47**, 694; V. THIAGARAJAN and N. VENKATSUBRAMANIAN, *Indian J. Chem.*, 1970, **8**, 809; N. S. SRINIVASAN and N. VENKATSUBRAMANIAN, *Indian J. Chem.*, 1971, **9**, 726; 1972, **10**, 1014; S. P. MUSHRAN, J. N. TIWARI, A. K. BOSE and K. SINGH, *Indian J. Chem., Sect. A*, 1978, **16**, 35; G. GOPALKRISHNAN, B. R. PUL, and N. VENKATSUBRAMANIAN, *Indian J. Chem., Sect. B*, 1980, **19**, 293; J. P. SHARMA, R. N. P. SINGH, A. K. SINGH and B. SINGH, *Tetrahedron*, 1986, **42**, 2739, and the references therein; P. S. R. MURTHY, C. JANARDHANA, G. P. BEHERA and G. K. MOHANTY, *Int. J. Chem. Kinet.*, 1982, **14**, 801.
3. P. SAROJA, B. K. KUMAR and S. KANDLIKAR, *Indian J. Chem., Sect. A*, 1989, **28**, 501.
4. K. J. P. ORTON and A. E. BRADFELD, *J. Chem. Soc.*, 1924, 640; 1927, 983.
5. "Determination of Organic Structures by Physical Methods", eds BROWN, MCDANIEL and HAWLINGER in Brande and Nachod, **1**, 567-662(1955), Academic, New York, 1955, Vol. 1, pp. 567-662.
6. E. S. AMIS, "Solvent Effects on Reaction Rates and Mechanisms", Academic, New York, 1967.
7. R. W. TAFT in "Steric Effects in Organic Chemistry", ed. M. NEWMAN, Wiley, New York, 1956, Chap. 13.
8. O. EXNER, *Collect. Czech. Chem. Commun.*, 1964, **29**, 1094.