

## Role of Structure, Medium and Pathway in Electrophilic Aromatic Substitutions. Part 2.<sup>1</sup> Incidence of $\pi$ -Complexes and Influence of Medium on Stability of Incipient Moieties in Molecular Chlorination of Aromatic Hydrocarbons

Osman M. E. El-Dusouqui,\* Karima A. M. Mahmud and Yousif Sulfab

Department of Chemistry, University of Kuwait, PO Box 5969 Safat, 13060 Safat, Kuwait

The kinetics of molecular chlorination of twelve benzenoid compounds has been studied at 25 °C in pure acetic acid as solvent, and over a wide range of initial substrate concentrations. For each kinetic run the rate coefficient remains constant to within experimental error. However, in the case of eleven of these compounds a significant sustained decrease in the rate coefficient of the substrate is observed to follow a regular increase in initial substrate concentration. For example, the rate constant of *p*-xylene decreases steadily to effect a 55% rate drop ( $k_2 = 3.42\text{--}1.55 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) over a tenfold increase in initial xylene concentration (0.191–1.98 mol dm<sup>-3</sup>). The results obtained in the present kinetic study are amenable to: (i) qualitative interpretation in terms of a differential effect of solvent on incipient charged moieties associated with the transition state of the reaction; and (ii) quantitative rationalization when a pathway is accepted in which a pre-equilibrium  $\pi$ -complex precedes the transition state, and with the kinetic rate equation incorporating both the equilibrium constant of the complex and its specific rate of further reaction.

Molecular halogenation of aromatic compounds is a well documented reaction, and its overall mechanism is known.<sup>2</sup> However, the involvement of  $\pi$ -complexes as discrete entities along electrophilic reaction pathways,<sup>3,4</sup> which has met with criticism,<sup>5</sup> has recently received favourable attention. For example, the work of Kochi has shown that rates of electrophilic molecular halogenation reactions correlate well with transition energies of charge-transfer arene-halogen complexes.<sup>6</sup> This work has also emphasized the importance of solvation phenomena in electrophilic reactions involving charged cationic intermediates. A novel approach to this problem was that of Bellucci, who reported an inverse effect of temperature and substrate concentration on the rate constant of molecular bromination of cyclohexene.<sup>7</sup> This observation was used by Bellucci to postulate charge-transfer complexes as key intermediates for such reactions. Charge-transfer complexes were previously considered to be an important unifying factor in the halogenation reactions of both alkenes and arenes.<sup>6</sup>

Nine of the arenes used in the present investigation are alkylbenzenes. Rationalization of the reactivity of these aromatic hydrocarbons often invokes hyperconjugative effects, and the possible role of solvent and steric factors in influencing the magnitude of conjugative contribution to reactivity from the C–H and C–C  $\sigma$ -bonds of the alkyl substituents.<sup>8</sup> Rate constants of halogenation reactions of aromatic hydrocarbons have previously been observed to vary with change in initial substrate concentration.<sup>9–12</sup> A substantial rate reduction has also been noted for chlorobenzene.<sup>13</sup> However, no systematic study of this phenomenon has been undertaken, and an attempt at an explanation of the origin of the effect has only been offered in passing.<sup>14</sup>

### Results and Discussion

**Reaction Kinetics.**—The rates of reaction of all the compounds studied here were of second-order overall, and first-order with respect to both chlorine and substrate. Literature rate constants have been reproduced for a number of these compounds under comparable initial substrate concentrations.<sup>9,10,15,16</sup> To safeguard against any competitive

dichlorination, kinetic experiments were run using substrate concentrations at about ten times those of chlorine. The rate constants were calculated both graphically and by using the integrated rate equation for second-order reactions. Rate coefficients of individual kinetic runs remained constant for each run and gave experimental errors of the order of  $\pm 0.4\text{--}6.5\%$ . For naphthalene, *tert*-butylbenzene and *p*-di-*tert*-butylbenzene, kinetic runs which showed experimental error in excess of  $\pm 3\%$  were excluded from the present analysis.

The second-order rate constants obtained under the conditions of this study are summarized in Table 1. The effect of change of initial substrate concentration on the magnitude of reaction rate constants is very large. On the other hand, change in the concentration of chlorine is found to have no significant effect on rate coefficients.<sup>9</sup>

**Qualitative Rationalization of Kinetic Results.**—Change of reaction medium affects molecular halogenation of aromatic compounds.<sup>9</sup> The roles suggested for the solvent include assistance in the cleavage of the inter-halogen bond in the intermediate complex, and solvation of charged reactive species.<sup>6,16,17</sup> For alkylbenzenes, the polarity and solvation power of the medium are crucial to substrate reactivity. Contribution to reactivity from alkyl substituents is known to involve hyperconjugative electron release to the electron-deficient transition state and the arenonium  $\sigma$ -complex intermediate.<sup>8,18</sup> This mode of conjugative  $\sigma$ -bond electron participation necessitates the development of partial positive charge on incipient protons and methyl carbocations from the alkyl groups. Solvation of the incipient charged moieties would lead to charge dispersion and consequently to enhanced substrate reactivity. This reactivity would decrease if the solvating power of the medium diminishes. Alkylbenzenes would, as covalent hydrocarbons, be expected to have an adverse effect on the polarity and solvating ability of acetic acid.<sup>14</sup> Further, solvation of the incipient bulkier cationic alkyl moieties is less accessible compared with solvation of the smaller incipient proton.<sup>8,12</sup> Accordingly, changes in the polarity of the medium would have larger effects on the reactivity of the methylbenzenes (incipient protons in a methyl group

**Table 1** Effect of concentration and of added benzene on rate coefficients ( $k_2/10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) of molecular chlorination reactions

[Toluene] <sup>a</sup> /mol dm <sup>-3</sup> $k_2/10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0.100 0.68	0.179 0.58	0.209 0.55	0.714 0.40	1.034 0.37	1.504 0.27	2.060 0.24
[Ethylbenzene]/mol dm <sup>-3</sup> $k_2/10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0.104 0.43	0.203 0.38	0.705 0.26	1.020 0.23			
[Cumene]/mol dm <sup>-3</sup> $k_2/10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0.203 0.29	0.215 0.25	0.700 0.18				
[ <i>tert</i> -Butylbenzene] <sup>b</sup> /mol dm <sup>-3</sup> $k_2/10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0.102 0.185	0.207 0.172	0.710 0.165	1.033 0.153			
[ <i>o</i> -Xylene]/mol dm <sup>-3</sup> $k_2/10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0.190 3.38	0.201 3.24	0.994 2.80	1.988 1.69			
[ <i>p</i> -Xylene]/mol dm <sup>-3</sup> $k_2/10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0.191 3.42	0.215 3.36	0.319 3.16	0.461 2.97	0.700 2.64	1.980 1.55	
[ <i>m</i> -Xylene]/mol dm <sup>-3</sup> $k_2/10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0.605 × 10 <sup>-2</sup> 285		2.04 × 10 <sup>-2</sup> 250				
[ <i>p-tert</i> -Butyltoluene]/mol dm <sup>-3</sup> $k_2/10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0.0205 3.41	0.155 2.36	0.194 2.20	0.200 2.16			
[ <i>p</i> -Di- <i>tert</i> -butylbenzene]/mol dm <sup>-3</sup> $k_2/10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0.155 0.435	0.200 0.410					
[Naphthalene]/mol dm <sup>-3</sup> $k_2/10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0.0300 5.90	0.150 5.70	0.300 5.50				
[Biphenyl]/mol dm <sup>-3</sup> $k_2/10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0.0505 0.74	0.102 0.72	0.200 0.69				
[ <i>p</i> -Chloroacetanilide] <sup>c</sup> /mol dm <sup>-3</sup> $k_2/10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0.0205 6.46		0.100 6.42				

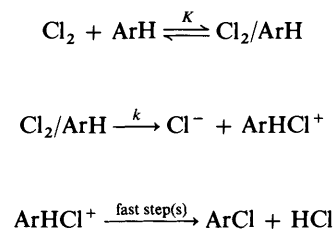
<sup>a</sup> With [toluene] = 0.200 mol dm<sup>-3</sup> and [benzene] = 0.800 mol dm<sup>-3</sup>,  $k_2 = 1.70 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . <sup>b</sup> With [*tert*-butylbenzene] = 0.200 mol dm<sup>-3</sup> and [benzene] = 0.800 mol dm<sup>-3</sup>,  $k_2 = 1.76 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . <sup>c</sup> With [*p*-chloroacetanilide] = 0.200 mol dm<sup>-3</sup> and [benzene] = 0.800 mol dm<sup>-3</sup>,  $k_2 = 4.98 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

environ) than on the reactivity of *tert*-butylbenzenes (incipient methyl carbocations in the confines of a *tert*-butyl group); the effect on ethylbenzene and cumene being intermediate.

The present kinetic results seem to be in accord with the above exposition. Estimations from the rate data of Table 1 revealed the following pattern of appreciable decrease in reactivity following a tenfold increase in initial substrate concentration: toluene (46–56%), ethylbenzene (46%), *o*-xylene (48%) and *p*-xylene (55%). However, the corresponding rate reduction for *tert*-butylbenzene at 17% appears to be significantly smaller by comparison. This kinetic behaviour is also evident from the results obtained for *p-tert*-butyltoluene, *m*-xylene, cumene, *p*-di-*tert*-butylbenzene, naphthalene and biphenyl. It is to be noted, however, that the concentration ranges over which the percentage decrease in  $k_2$  values was evaluated are closest for the monoalkylbenzenes and for *o*- and *p*-xylene. The results for the remaining substrates, although reported for varied concentration ranges, nevertheless seem to be consistent with the observed trend. Benzene (non-polar and inert to chlorination under the present kinetic conditions) reduced the rate coefficient of molecular chlorination of toluene when added in lieu of an equivalent increase in substrate concentration, but seems to have no pronounced effect on the  $k_2$  value of *tert*-butylbenzene. Interestingly, the reactivity of *p*-chloroacetanilide, which was unaffected by an increase in substrate concentration, diminished substantially when benzene was added to replace 80% of the concentration of the anilide. This change in reactivity might be related to a solvent effect on N–H hyperconjugation involving the acetamido group.

*Quantitative Analysis of Kinetic Results.*—An alternative

interpretation of the observed kinetic phenomenon has been outlined in a previous communication.<sup>1</sup> The analysis is based on an earlier postulation<sup>3–7</sup> that a pre-equilibrium  $\pi$  (charge-transfer; encounter) complex precedes the transition state and the arenonium  $\sigma$ -complex intermediate typical of electrophilic molecular halogenation pathways. The pre-equilibrium  $\pi$ -complex is taken to represent an association of molecular chlorine and the aromatic substrate,  $\text{Cl}_2/\text{ArH}$  (Scheme 1).

**Scheme 1**

The equilibrium set-up, and the rate equation formulation follow Scheme 2, where *f* denotes free (uncomplexed) reactants,

$$[\text{Cl}_2/\text{ArH}] = K[\text{Cl}_2]_f[\text{ArH}]_f$$

$$\text{Rate} = k[\text{Cl}_2/\text{ArH}] = kK[\text{Cl}_2]_f[\text{ArH}]_f$$

**Scheme 2**

and  $[\text{Cl}_2/\text{ArH}]$  is the equilibrium concentration of the  $\pi$ -complex; total concentrations of reactants carry the subscript

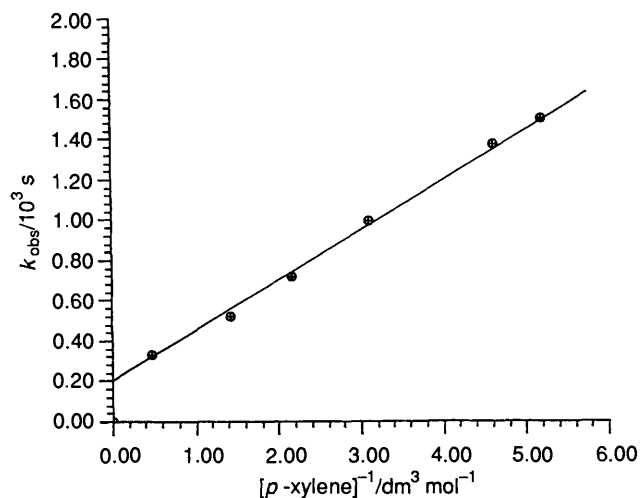


Fig. 1 Reciprocal of observed first-order rate constant vs. inverse of initial *p*-xylene concentration

Table 2 Equilibrium constants and rates of further molecular transformation of  $\pi$ -complexes of aromatic hydrocarbons

Hydrocarbon	$K/\text{dm}^3 \text{ mol}^{-1}$	$k/10^{-4} \text{ s}^{-1}$
Toluene	$1.2 \pm 0.2$	$6.3 \pm 0.9$
Ethylbenzene	$1.5 \pm 0.1$	$5.0 \pm 0.3$
<i>tert</i> -Butylbenzene	$6.0 \pm 1.2$	$1.9 \pm 0.04$
<i>o</i> -Xylene	$0.44 \pm 0.1$	$82.0 \pm 2.6$
<i>p</i> -Xylene	$0.73 \pm 0.05$	$53.8 \pm 4.0$
<i>p-tert</i> -Butyltoluene	$3.0 \pm 0.2$	$11.8 \pm 0.8$
Naphthalene	$0.17 \pm 0.02$	$3390 \pm 390$

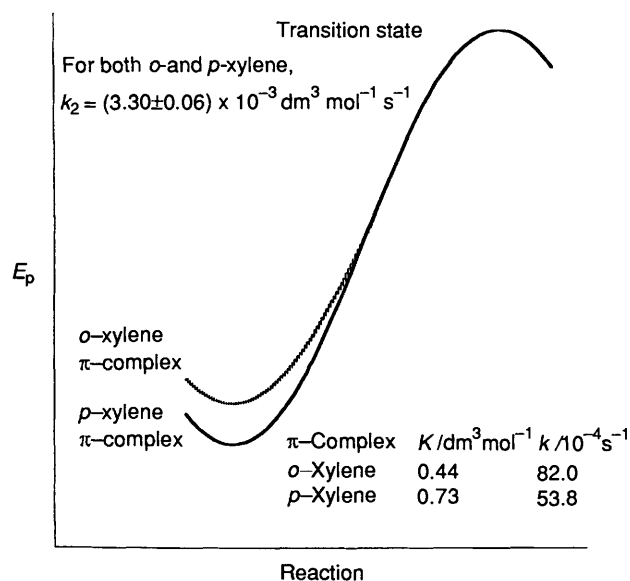
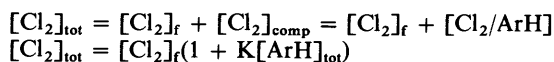


Fig. 2 Part of reaction/energy profile diagram for molecular chlorination of *o*- and *p*-xylene

(tot). Since the concentration of the aromatic substrate is in large excess it is assumed that  $[\text{ArH}]_f \approx [\text{ArH}]_{\text{tot}}$ , and substituting the equilibrium concentration of the  $\pi$ -complex for complexed chlorine,  $[\text{Cl}_2]_{\text{comp}}$ , gives the relations in Scheme 3.



Scheme 3

The rate equation could now be presented in the form given in eqn. (1).

$$\text{Rate} = k K[\text{Cl}_2]_{\text{tot}}[\text{ArH}]_{\text{tot}}/(1 + K[\text{ArH}]_{\text{tot}}) \quad (1)$$

Since the reaction is first-order with respect to chlorine, a relation for the observed kinetic rate constant is given by eqns. (2) and (3).

$$k_{\text{obs}} = k K[\text{ArH}]_{\text{tot}}/(1 + K[\text{ArH}]_{\text{tot}}) \quad (2)$$

$$k_{\text{obs}}^{-1} = k^{-1} + (k K[\text{ArH}]_{\text{tot}})^{-1} \quad (3)$$

In eqn. (2), the rate expression adequately explains the inverse relation of rate constant to initial substrate concentration, with the magnitude of  $K$  determining the extent of the rate reduction per substrate (Table 1). Eqn. (3) is used to compute the values of both  $k$  and  $K$  from the intercept and slope of a plot of the reciprocals of the observed first-order rate constant and the corresponding initial substrate concentration; the observed second-order constants (Table 1) are normalized to observed  $k_1$  values for this purpose. A typical plot is shown in Fig. 1 for *p*-xylene, and a similar treatment of the kinetic results for toluene has been reported earlier.<sup>1</sup> The values of  $k$  and  $K$  thus calculated for naphthalene and six alkylbenzenes are listed in Table 2. Computations of  $k$  and  $K$  were made using linear regression analysis with the absolute values of the correlation coefficients scaling 0.996 82–1.0000.

The postulation of a  $\pi$ -complex as a discrete entity along the chlorination reaction pathway might require further justification.<sup>6,7</sup> Within this context, the present kinetic analysis offers three helpful observations in support of the notion of  $\pi$ -complexes as key intermediates in molecular chlorination of benzenoid compounds. Besides, alkylbenzenes were noted to have high donor-acceptor basicities.<sup>19</sup>

(a) Zollinger has shown that bulky substituents promoted  $\pi$ -complex formation apparently through hindrance of molecular transformations from the more trigonal structure of a  $\pi$ -complex to a more tetrahedral *ipso*-position in the  $\sigma$ -complex.<sup>3</sup> This observation is borne out by the present findings. The results in Table 2 show higher  $K$  values for *tert*-butylbenzene > ethylbenzene > toluene and the reverse order for their  $k$  values of further transformation. The same applies in the case of *p-tert*-butyltoluene and either *o*- or *p*-xylene.

(b) The observed rate constants of *o*- and *p*-xylene are the same [ $k_2 = (3.30 \pm 0.06) \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at  $0.2 \text{ mol dm}^{-3}$  substrate concentration]. This allows the representation of the transition states of these two structurally related alkylbenzenes by the same energy maxima in a reaction/energy profile diagram (Fig. 2). The values calculated (Table 2) for the equilibrium constants ( $K/\text{dm}^3 \text{ mol}^{-1}$ ) of *p*-xylene and *o*-xylene are 0.73 and 0.44, respectively. Since the  $\pi$ -complex of *p*-xylene is seen to be more stable than the  $\pi$ -complex of *o*-xylene, the former  $\pi$ -complex would require more activation energy to surmount the transition state energy barrier and would, therefore, give the lower rate of further reaction. The  $k$  values obtained are, respectively, 53.8 and 82.0  $\text{s}^{-1}$ . This kinetic relationship would presumably hold where the  $\pi$ -complex appears as an entity along the reaction coordinate.

(c) An important outcome of the present study is a linear correlation involving the free energies of reaction and activation relating, respectively, to  $K$  and  $k$  and to the two key  $\pi$ - and  $\sigma$ -complexes.<sup>20</sup> Besides, this linear free energy relationship is evidently structure-dependent. Fig. 3 shows two linear plots: one correlating  $K$  and  $k$  for monoalkylbenzenes, the other is for dialkylbenzenes. This finding further reinforces the other two observations outlined above.

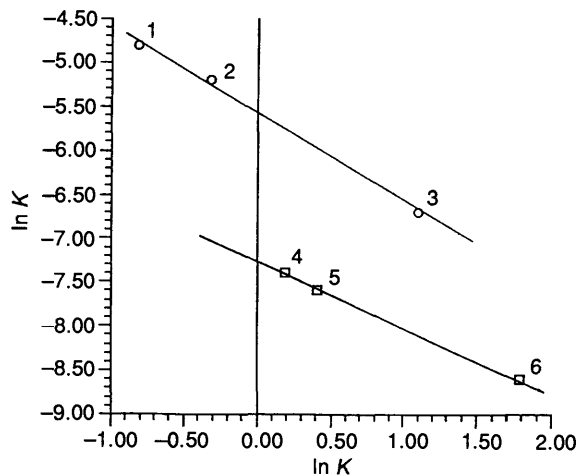


Fig. 3 Plot of  $\ln k$  vs.  $\ln K$  of  $\pi$ -complexes of alkylbenzenes 1–6: respectively, *o*-xylene, *p*-xylene, *p*-*tert*-butyltoluene, toluene, ethylbenzene and *t*-butylbenzene

### Experimental

**Purification and Characterization of Materials.**—Analytical grade acetic acid (Fluka) was used without further purification. The acid was stable to both molecular chlorine and bromine; m.p. 16.55 °C (lit.,<sup>21</sup> 16.6 °C). Liquid substances were fractionally distilled to obtain pure middle cuts. Purity was checked by b.p. and GLC analysis. *p*-Xylene was purified through fractional crystallization followed by fractional distillation. The recorded boiling points of benzene, toluene, *tert*-butylbenzene, the xylenes, *p*-*tert*-butyltoluene, ethylbenzene and cumene were identical with literature values.<sup>21</sup> Naphthalene, biphenyl, *p*-chloroacetanilide and *p*-*di-tert*-butylbenzene were recrystallized from ethanol until purity judged from m.p. and GLC analysis was attained.<sup>21</sup> Chlorine gas (Merck) was freed from HCl and moisture before use.

**Rate Measurements.**—Chlorination reactions were carefully shielded from light. Rates were determined iodometrically by following chlorine uptake during the course of a kinetic run.<sup>22</sup> Solutions of reactants and reaction admixtures were kept at a constant temperature of  $25.0 \pm 0.1$  °C. Shallow two-cavity glass reactors were used to follow the kinetics of the fast-reacting naphthalene: the reactants were quickly mixed in one cavity and immediately quenched with KI solution kept in the second cavity. The procedure for evaluating the rate constants has been described.<sup>22</sup>

### Acknowledgements

Research grant No. SC006 received from the University of Kuwait is gratefully acknowledged. The principal author is indebted to Professor Johannes Lercher and the Institute of Physical Chemistry, Technical University of Vienna, for their help and support.

### References

- 1 Part 1, O. M. E. El-Dusouqui, K. A. M. Mahmud and Y. Sulfab, *Tetrahedron Lett.*, 1987, **28**, 2417.
- 2 R. O. C. Norman and R. Taylor, *Electrophilic Substitution in Benzenoid Compounds*, Elsevier, Amsterdam, 1965.
- 3 M. Christen and H. Zollinger, *Helv. Chim. Acta*, 1962, **45**, 2057, 2066; M. Christen, W. Koch, W. Simon and H. Zollinger, *Helv. Chim. Acta*, 1962, **45**, 2077.
- 4 G. A. Olah, *Proceedings of the Chemical Society Organic Reaction Mechanisms Symposium*, The Chemical Society, London, 1965, p. 21.
- 5 D. V. Banthorpe, *Chem. Soc. Rev.*, 1970, **70**, 295; and relevant references therein.
- 6 S. Fukuzumi and J. K. Kochi, *J. Am. Chem. Soc.*, 1982, **104**, 7599.
- 7 G. Bellucci, R. Bianchini and R. Ambrosetti, *J. Am. Chem. Soc.*, 1985, **107**, 2464.
- 8 E. Glyde and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1977, 678; and relevant references therein.
- 9 H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, 1957, **79**, 5175.
- 10 L. M. Stock and H. C. Brown, *J. Am. Chem. Soc.*, 1959, **81**, 5615.
- 11 R. M. Keefer, A. Ottenburg and L. J. Andrews, *J. Am. Chem. Soc.*, 1956, **78**, 255; 3637.
- 12 L. M. Stock and A. Himoe, *J. Am. Chem. Soc.*, 1961, **83**, 1937.
- 13 L. M. Stock and F. W. Baker, *J. Am. Chem. Soc.*, 1962, **84**, 1661.
- 14 P. B. D. de la Mare and M. Hassan, *J. Chem. Soc.*, 1958, 1519.
- 15 M. J. S. Dewar and T. Mole, *J. Chem. Soc.*, 1957, 342.
- 16 R. J. Dolinski and R. M. Nowak, *J. Org. Chem.*, 1969, **34**, 3342.
- 17 L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, 1959, **81**, 1063.
- 18 T. J. Broxton, L. W. Deady, A. R. Katritzky, A. Liu and R. D. Topsom, *J. Am. Chem. Soc.*, 1970, **92**, 6845.
- 19 H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.*, 1952, **74**, 3570; R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, 1955, **77**, 2164.
- 20 F. Wilkinson, *Chemical Kinetics and Reaction Mechanisms*, Van Nostrand Reinhold, London, 1980, p. 164.
- 21 *CRC Handbook of Chemistry and Physics*, ed. R. C. Weast, CRC Press, Cleveland, 1978.
- 22 O. M. E. El-Dusouqui and M. Hassan, *J. Chem. Soc. B*, 1966, 374.

Paper 0/05830K

Received 31st December 1990

Accepted 4th April 1991