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POLAR EFFECTS IN HYDROGEN ABSTRACTION FROM BENZALDEHYDES—III

RADICAL CHLORINATION BY SULPHURYL CHLORIDE

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Abstract—The relative rates of radical chlorination of *m*- and *p*- substituted benzaldehydes with sulphuryl chloride at 40° in CCl_4 have been determined by means of a competitive reaction using *p*-diethylbenzene as reference standard. The relative reactivities were calculated from the amounts of aroyl chloride and α-chloro-*p*-diethylbenzene found and a polar effect ($\rho = -0{\cdot}53$) was shown to be correlated by the Hammett equation with the σ constants. A comparison of the ρ-values with the redetermined value ($\rho = -1{\cdot}13$) at the same temperature for bromotrichloromethane with the same system shows that radical halogenation with SO_2Cl_2 is much less selective than with $BrCCl_3$.

IN PART 1[1] it was found that the formation of substituted benzoyl radicals by abstraction from benzaldehyde by the trichloromethyl radical obey the Hammett $\rho\sigma$ relationship. Recently a similar investigation[2] with the trichloromethane sulphonyl radical towards benzaldehydes has also demonstrated a polar effect, the ρ-value found being significantly different from that reported[1] for the $\cdot CCl_3$ radical. The study of polar effects in hydrogen-abstraction from benzaldehydes has now been extended to radical chlorination with sulphuryl chloride. The competitive sulphuryl chloride chlorination of benzaldehyde in presence of *p*-xylene, ethylbenzene and *p*-diethylbenzene has been investigated recently[3] and the reactivity values relative to the α-position of these hydrocarbons reported were 5·16, 5·62 and 2·51, respectively, at 40° in CCl_4 solution. In the present work the radical chlorination of the substituted benzaldehydes was carried out at 40° under similar conditions using *p*-diethylbenzene as reference compound. The substituent effect in the bromination of benzaldehydes by bromotrichloromethane have been re-investigated at this temperature in order that the magnitude of the ρ-values for these two halogenating agents can be compared.

RESULTS AND DISCUSSION

The reactivities of seven *m*- and *p*-substituted benzaldehydes and the parent compound relative to that of the benzylic hydrogen atoms of *p*-diethylbenzene toward sulphuryl chloride have been measured. The aroyl chlorides were estimated by IR spectrophotometry[2,3] and the total labile chlorides ($ArCOCl + p\text{-}EtC_6H_4CHClCH_3$) determined by Volhard's method after reaction with aniline.[3] Typical results are given in Table 1 where the unconsumed aldehydes estimated[2,3] show good material balance for the initial aldehydes used. The total labile chlorides found averaged 90 ±2% of the SO_2Cl_2 used, in good agreement with the 90·6% reported[3] for competitive experiments using benzaldehyde and ethylbenzene in which β-chloroethylbenzene was found not to interfere with the estimation of the total labile chlorides. Thus

β-chlorination of p-diethylbenzene does not affect the measured relative reactivity values of the substituted benzaldehydes investigated.

The reactivity of the benzaldehydes relative to the α-position of p-diethylbenzenes, $K/K_{\alpha-DEB}$ were calculated by the usual relative rate equation[1] and the effects of substituents of benzaldehyde toward sulphuryl chloride are given in Table 2. Application of the Hammett equation, by standard statistical methods,[4] shows that the results are better correlated by the σ constants of McDaniel and Brown,[5] with $\rho = -0{\cdot}53 \pm 0{\cdot}03$ (corr coeff = 0·981), than by the σ^+ constants of Brown and Okamoto[6] ($\rho = -0{\cdot}30 \pm 0{\cdot}07$; r = 0·890). The present results confirm the presence of polar effect ($\rho = -0{\cdot}48$ based on 4 electron withdrawing substituents) reported by Arai[7] in the absence of any solvent other than the standard substrate toluene at 80°.

The reactivities of substituted benzaldehydes and the parent compound relative to ethylbenzene towards bromotrichloromethane[1] have been redetermined at 40° and the results are given in Table 3. For m- and p-methylbenzaldehydes minor corrections[1] were applied to take account of methyl C—H abstraction as previously described. The ratio of the reactivity of the aldehydic C—H to that of the methyl C—H was found to be 25·3 ± 0·7 and 21·0 ± 1·3 per molecule for the m- and p-isomers, respectively. The reactivity value K_{PhCHO}/K_{PhEt} determined was 2·41 compared to a value of 1·20 at 80°, a result consistent with the greater selectivity of the radical at a lower temperature. Again the p-MeO and p-PhO values were explicably[1] low and have been omitted from the correlation by the Hammett equation. Like the results ($\rho = -0{\cdot}74$) found at 80° the present data are also well correlated by the σ constants, with $\rho = -1{\cdot}13 \pm 0{\cdot}01$ (corr coeff = 0·998) compared to the correlation with the σ^+ constants ($\rho = -0{\cdot}96 \pm 0{\cdot}07$, r = 0·971). The more negative ρ-value at 40° is to be expected as selectivity in hydrogen-abstraction by radicals can be increased by lowering the temperature.

It has been shown[8] that the trichloromethyl radical is highly selective in benzylic hydrogen abstraction and thus a fairly large polar effect is to be expected even in a relatively reactive substrate like benzaldehyde.[8b] A qualitative comparison of the magnitude of the polar effects in the benzaldehyde series towards $BrCCl_3$, Cl_3CSO_2Cl and SO_2Cl_2 can be seen from the ρ-values of $-1{\cdot}13$ (40°), $-0{\cdot}54$ (80°)[2] and $-0{\cdot}53$ (40°), respectively, all correlated by the σ constants. The principal hydrogen-abstracting species with the first two reagents appear well established. Comparing the two chlorinating agents the ρ-value for sulphuryl chloride seems to be of the correct order of magnitude as it is known that SO_2Cl_2 is less selective than Cl_3CSO_2Cl in the chlorination of alkanes.[9]

The sulphuryl chloride chlorination of substituted toluenes[3] in dilute CCl_4 solution at 40° gave a ρ-value of $-0{\cdot}56$ which is significantly different from the ρ-value of $-0{\cdot}76$ at 70° reported[10] for photochlorination in the absence of a solvent. The latter result has been attributed[3] to the π-complexed Cl atom as the principal hydrogen-abstracting species. In the former case the $\cdot SO_2Cl$ radical has been cited as the main hydrogen-abstracting species, but any involvement of atom chlorine-chain could not be ruled out. Since the competitive chlorination of the benzaldehydes and p-diethylbenzene by SO_2Cl_2 has been carried out in dilute CCl_4 solution the $\cdot SO_2Cl$ radical could be similarly cited as the principal hydrogen-abstracting species without ruling out the possibility of Cl atoms being involved. Wiberg and Slaugh[11] found that the deuterium isotope effect, K_H/K_D for the chlorination of α-d_1-toluene by SO_2Cl_2 at

TABLE 1. TYPICAL RESULTS OF COMPETITIVE REACTION OF X-C_6H_4CHO AND p-EtC_6H_4Et WITH SO_2Cl_2[a] AT 40°

Aldehyde	Irradiation Time hr	Unreacted ArCHO, mmole	ArCOCl mmole	Mole % Initial ArCHO accounted	ArCOCl + α-chloride mmole	Rel. reactivity[b] $K_{ArCHO}/K_{\alpha\text{-DEB}}$
PhCHO	1·5	4·19	5·86	100·5	8·84	2·49
PhCHO	1·5	4·14	6·07	102	9·14	2·54
PhCHO	1·5	4·05	6·04	101	9·14	2·50
p-ClC_6H_4CHO	1·5	4·05	5·85	99	9·25	2·12
p-ClC_6H_4CHO	1·25	4·01	5·89	99	9·25	2·16
p-ClC_6H_4CHO	1·25	4·16	5·79	99·5	9·08	2·17
m-ClC_6H_4CHO	1·5	4·78	5·10	99	8·97	1·46
m-ClC_6H_4CHO	1·75	4·68	5·06	97	8·87	1·47
m-ClC_6H_4CHO	1·5	4·65	5·15	98	9·00	1·49

[a] ArCHO : p-EtC_6H_4Et : SO_2Cl_2 = 10 : 10 : 10 mmole in ca. 25 ml CCl_4.

[b] Calculated by the relative rate equation as in Ref 1.

TABLE 2. RELATIVE REACTIVITY OF SUBSTITUTED BENZALDEHYDES TOWARDS SO_2Cl_2 AT 40°

Substituent	p-PhO	p-MeO	p-Bu^t	none	m-MeO	p-Cl	m-F	m-Cl
$K/K_{\alpha\text{-DEB}}$	3·43 ±0·07	3·54 ±0·10	3·28 ±0·09	2·51 ±0·02	2·23 ±0·03	2·15 ±0·02	1·59 ±0·01	1·47 ±0·02
K/K_0	1·37	1·41	1·31	1·00	0·89	0·86	0·63	0·59

TABLE 3. RELATIVE REACTIVITY OF SUBSTITUTED BENZALDEHYDES TOWARDS THE TRICHLOROMETHYL RADICAL AT 40°

Substituent	p-PhO	p-MeO	p-Bu^t	p-Me[a]	m-Me[a]	none	p-Cl	m-Cl	m-Br
K/K_{PhEt}	2·57 ±0·08	2·35 ±0·04	3·87 ±0·07	3·64 ±0·07	2·95 ±0·03	2·41 ±0·05	1·24 ±0·03	0·89 ±0·03	0·87 ±0·02
K/K_0	1·07	0·98	1·61	1·51	1·22	1·00	0·52	0·37	0·36

[a] Corrected for methyl C—H abstraction.

77° in CCl_4 is only 10% higher than that found for molecular chlorine under similar conditions. Thus if the A factors in the Arhenius equation are similar the activation energy for the hydrogen-abstraction step by both atomic chlorine and the $\cdot SO_2Cl$ radical from substituted benzaldehydes should be almost identical, and the ρ-value would not be significantly affected even if atomic chlorine has been doing part of the hydrogen-abstraction.

EXPERIMENTAL

Materials. Sulphuryl chloride (Fluka puriss grade) stored in a darkened dessicator was used without purification. β-Chloroethylbenzene (Eastman Kodak and neophyl chloride (Fluka) was redistilled before use. α-Chloro-p-diethylbenzene was prepared from the corresponding alcohol and thionyl chloride.

p-Diethylbenzene was synthesized and purified as previously described. Aromatic aldehydes and other materials used were purified in the usual manner.[1]

Competitive reaction of benzaldehydes and p-*diethylbenzene with* SO_2Cl_2. These were carried out in CCl_4 soln at 40° as described.[3] The reaction was followed to complete consumption (1–2 hr) of SO_2Cl_2 by the disappearance of the 1420 cm^{-1} peak. Aroyl chlorides and unconsumed aromatic aldehydes were analysed[2, 3] by the IR method. The total labile chlorides ($ArCOCl + p\text{-}EtC_6H_4CHClCH_3$) were estimated by titrimetry.[3] With authentic mixtures the accuracy of the method was ±2% without implication of added *β*-chloroethylbenzene or neophyl chloride. Some typical results are given in Table 1.

Competitive reactions of substituted benzaldehydes and ethylbenzene with $BrCCl_3$ *at* 40°. These were performed in CCl_4 as in part I, and correction factors at this temp for abstraction from Me groups in *m*- and *p*-methylbenzaldehydes were also determined. All experiments were carried out in triplicate and the results are presented in Table 3.

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