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Mechanistic Studies in Strongly Basic Media. Part IV.¹ Proton Removal from 4-Nitrodiphenylmethyl Chloride by Sodium and Potassium t-Butoxides in t-Butyl Alcohol

By D. Bethell and A. F. Cockerill

Rates of proton abstraction from the a-carbon atom of 4-nitrodiphenylmethyl chloride in solutions of sodium and potassium t-butoxides in t-butyl alcohol at 30° have been measured spectrophotometrically. For a given concentration of base, the rate of attainment of equilibrium is faster when potassium is the counter-ion than when sodium t-butoxide is used. However, rates of proton abstraction in media having a given value of the indicator acidity function H_r^{BuOH} are independent of the nature of the cation. Mechanistic implications of the results are discussed.

PREVIOUS Parts ^{1,2} have used correlations of velocity constants for base-promoted reactions in t-butyl alcohol with medium basicity as measured by the extent of conversion of aromatic amine indicators into their conjugate bases and formalised in the acidity function $H_r^{BuOH.3}$ For solutions of alkali-metal t-butoxides (up to 0.1M) in t-butyl alcohol, such correlations were slightly different according to the nature of the re-Thus, for bifluorenylidene formation from action. substituted 9-bromofluorenes, log k_{obs} was a linear function of H_r^{BuOH} * with a slope close to unity irrespective of whether the conjugate base of the 9-bromofluorene underwent unimolecular decomposition⁴ or reacted with another 9-bromofluorene molecule in the

* log k_{obs} was originally correlated with log ([ArNH⁻]/[ArNH₂]), where ArNH₂ is an indicator, and $H_r^{BuOH} = \log ([ArNH^-]/[ArNH_2]) + \text{constant.}$

rate-determining step.² On the other hand, for E2elimination of hydrogen bromide from 9-bromo-9,9'bifluorenyl, log k_{obs} was not in general well correlated by the indicator acidity function: although, when sodium and potassium t-butoxides were used as bases, linear plots of log k_{obs} against H_r^{BuOH} were obtained, the slopes were 0.7. In both types of reaction, change of the alkali-metal cation from potassium to sodium in media having the same value of H_{r}^{BuOH} halved the reaction rate. We now report our investigation of the correlation of log k_{obs} with H_r^{BuOH} for a third type of base promoted reaction, namely, simple proton abstraction from 4-nitrodiphenylmethyl chloride.

- ¹ Part III, D. Bethell and A. F. Cockerill, preceding Paper.
- ² D. Bethell, J. Chem. Soc., 1963, 666.
 ³ D. Bethell and A. F. Cockerill, J. Chem. Soc. (B), 1966, 913.
 ⁴ D. Bethell and A. F. Cockerill, Proc. Chem. Soc., 1964, 283.

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EXPERIMENTAL

Materials.—Solvents and bases were as previously described.³ 4-Nitrodiphenylmethyl chloride was prepared by chlorination of the alcohol using either thionyl chloride or zinc chloride and hydrogen chloride in dry ether. The crude product was purified by passage in light petroleum solution through a column of activated alumina. Refrigeration of light petroleum solutions for several days afforded the chloride in crystalline form, m. p. 43° (lit.,⁵ 43°).

Effect of Bases on 4-Nitrodiphenylmethyl Chloride.— Treatment of the chloride with alkali-metal t-butoxides in t-butyl alcohol quickly produced an intense red colour $(\lambda_{max.} 425 \text{ m}\mu; \epsilon \sim 35,000 \text{ at high base concentrations})$. Rapid neutralisation of the solution destroyed the colour, the ultraviolet spectrum of the solution then being almost identical with that of the starting material. Further addition of base restored the red colour.

Prolonged storage of solutions of 4-nitrodiphenylmethyl chloride with base in t-butyl alcohol under nitrogen, typically for five days at 30°, led to fading of the red colour and precipitation of a yellow-brown solid. Dilution of the reaction mixture with water and filtration gave solid material which was shown by thin-layer chromatography to be essentially one compound. After three recrystallisations from benzene-ethanol it had m. p. 197-199° (Found: C, 73.7; H, 4.5; N, 6.8. $C_{26}H_{18}N_2O_4$ requires C, 73.9; H, 4.3; N, 6.6%); λ_{max} 360 mµ (ε 14,700) and 265 mµ (ε 23,700) in ethanol-chloroform, consistent with its being 4,4'-dinitrotetraphenylethylene. Similar treatment of 4-nitrodiphenylmethyl chloride with potassium t-butoxide in air gave 4-nitrobenzophenone (81%) and the tetra-arylethylene (18%).

From these observations it is concluded that the red colour first produced from the chloride and base is that of the carbanion derived by proton removal from the α -carbon atom. The carbanion could then be transformed into the olefinic product by one of the two mechanisms already identified for related compounds.

Kinetic Studies of Carbanion Formation.—Because the rate of disappearance of the carbanion is very slow compared with its formation, the kinetics of carbanion formation could be studied spectrophotometrically without interference due to decomposition, provided that dilute ($<10^{-2}$ M) solutions of sodium or potassium t-butoxides in t-butyl alcohol were used. When benzyltrimethylammonium t-butoxide was used at concentrations down to 1.3×10^{-3} M, carbanion formation was complete before the first spectrophotometer reading could be taken (1 min.). The appearance of the carbanion colour was followed, usually at 425 mµ, using a Unicam S.P. 500 quartz spectrophotometer, reactions being carried out in the optical cell, the temperature of which was maintained at $30.0^{\circ} \pm 0.1^{\circ}$.

The formation of the carbanion can be expressed by the equation

$$RH + M^+OBu^- \xrightarrow{k_1} R^-M^+ + BuOH$$

Since the base was always in large excess compared with 4-nitrodiphenylmethyl chloride, the integrated kinetic equation is

2.303 log
$$\left\{ \frac{[R^-M^+]_e}{[R^-M^+]_e - [R^-M^+]_t} \right\} = k_{obs}t = (k_1[M^+OBu^-] + k_{-1}[BuOH])t$$

Square brackets indicate concentrations and the subscripts e and t refer to equilibrium and time t-respectively. Expressed in terms of optical density (D) of the reaction solution, the kinetic equation becomes

2.303 log $\{D_e/(D_e - D_t)\} = k_{obs}t$. Values of k_{obs} were derived graphically from the accurately rectilinear plots of $\log(D_e - D_t)$ against time. Results are recorded in Tables 1 and 2. Values of H_r^{BuOH} were interpolated from our previous measurements.³

Table	1
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Values of k_{obs} for carbanion formation from 4-nitrodiphenylmethyl chloride (RCl) and potassium t-butoxide in t-butyl alcohol at 30°

10 ⁵ [RCl] (м)	10 ⁴ [KOBu] (м)	k_{obs} (min. ⁻¹)	$H_{r}^{\rm BuOH}$
4.13	4.17	0.219	-1.10
2.26	6.36	0.307	-0.88
2.74	11.3	0.479	-0.58
1.13	12.7	0.585	-0.51
2.58	15.0	0.703	-0.43
4.53	19-1	0.852	-0.32
4.34	22.8	1.00	-0.53
1.13	25.4	1.04	0.18
4.42	30.5	1.27	-0.08
1.13	50.7	2.07	0.16

TABLE 2

Values of $k_{\rm obs}$ for carbanion formation from 4-nitrodiphenylmethyl chloride (RCl) and sodium t-butoxide in t-butyl alcohol at 30°

10 ⁵ [RCl] (м)	10 ⁴ [NaOBu] (м)	k _{obs} (min. ⁻¹)	$H_{ m r}^{ m BuOH}$
2.26	5.18	0.126	-1.33
$2 \cdot 26$	6.91	0.124	-1.18
1.13	17.3	0.412	-0.70
1.13	34.6	0.774	-0.33

RESULTS AND DISCUSSION

Graphs of k_{obs} against [MOBu] were linear for the two bases. From the slopes and intercepts of these lines, determined by the method of least squares, values of k_1 and k_{-1} [BuOH] were determined (Table 3).

TABLE 3

Kinetic parameters for carbanion formation from 4-nitrodiphenylmethyl chloride in t-butyl alcohol at 30°

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Base	KOBu	NaOBu
$\begin{array}{l} k_1 \ (l. \ mole^{-1} \ min.^{-1}) \ \dots \\ k_{-1} [BuOH] \ (min.^{-1}) \ \dots \\ K_b \ = \ k_1 / (k_{-1} [BuOH]) \ (l. \ mole^{-1}) \ \dots \end{array}$	$\begin{array}{r} 400 \\ 5.96 \times 10^{-2} \\ 6710 \end{array}$	$219 \\ 2 \cdot 23 \times 10^{-2} \\ 9830$

Clearly velocity constants for both the forward and back reactions are greater when potassium t-butoxide is the base than when sodium t-butoxide is used. From the second-order constant k_1 , pseudo-first-order constants for the forward reaction can be calculated by multiplication by the base concentration. A logarithmic plot of these pseudo-first-order constants agsinst H_r^{BuOH} is shown in the Figure. Points for both sodium and potassium t-butoxides fall on a single straight line of slope 0.82.

This behaviour is in marked contrast to that observed for reactions in which the rate-determining step involves reaction of a carbanion either in a unimolecular process or with a second species. In the present study, the ⁵ E. F. Brittain, G. Kohnstam, A. Queen, and B. Shillaker, J. Chem. Soc., 1961, 2045. pseudo-first-order velocity constant for reprotonation of the carbanion is some 2.7 times greater when the counter-ion is potassium than when it is sodium. In the conversion of 9-bromofluorenes into bifluorenylidenes, the reaction rate in media having the same value of H_r^{BuOH} is dependent on the nature of the cation. Preliminary results ⁶ on the base-promoted oxidation of



Dependence of pseudo-first-order velocity constants for proton removal from 4-nitrodiphenylmethyl chloride on H_r^{BuOH} for potassium (\bigcirc) and sodium (\bigcirc) t-butoxide

substituted fluorenes in t-butyl alcohol, in which the slow step is probably electron transfer from the 9-fluorenyl carbanion to oxygen,⁷ indicate that the reaction rate is cation-dependent. On the other hand, hydrogen isotope exchange at the 9-position in fluorene appears to be independent of the nature of the cation for a given value of $H_r^{\rm BuOH.6}$

⁶ R. J. E. Talbot, unpublished observations.

⁷ G. A. Russell and A. G. Bemis, *Chem. and Ind.*, 1965, 1262.
⁸ Cf. M. Anbar, M. Bobtelsky, D. Samuel, B. Silver, and G. Yagil, J. Amer. Chem. Soc., 1963, 85, 2380.

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We tentatively suggest therefore that dependence of reaction rates on $H_r^{\rm BuOH}$ alone may be characteristic of reactions in which carbanion formation is rate-limiting. If the observed velocity is that of a process in which a carbanion is a reactant, then, because of the apparent great importance of interionic interactions in t-butyl alcohol,³ at a given value of $H_r^{\rm BuOH}$ it will be dependent on the nature of the cation associated with the carbanion. This difference in behaviour may have applications as a mechanistic criterion in base-promoted organic reactions, particularly eliminations.¹

Dependence of log k on H_r^{BuOH} may not be unique for proton abstraction.⁸ Schaal and Peure⁹ have already shown that in displacement of a nitro-group from p-dinitrobenzene by lithium, sodium, or potassium methoxides in methanol, reaction rates are correlated by an H-type function. Nucleophilic aromatic substitution is generally thought to involve rate-determining co-ordination of the nucleophil to the aromatic nucleus, forming a so-called Meisenheimer complex.¹⁰ Schaal and Peure, however, interpreted their observations in terms of rate-determining decomposition of this intermediate complex, implying that activity coefficient ratios of the type $(f_{ArH} \cdot f_{B^-})/(f_{ArHOMe^-} \cdot f_{BH})$ are invariant with change in medium composition. While this may be so, correlation of velocity constants with a J-type function ¹¹ seems to be more appropriate to the mechanism suggested by Schaal and Peure. On the other hand, these results on replacement of aromatic nitrogroups by methoxyl fit well with the generalisation suggested above, if formation of the intermediate complex, a rather special type of carbanion, is rate-determining. Further examination of this question is necessary.

ROBERT ROBINSON LABORATORIES, THE UNIVERSITY,

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see also C. Vermesse-Jacquinot, J. Chim. phys., 1965, 62, 235. ¹⁰ J. Hine, "Physical Organic Chemistry," 2nd edn., McGraw-

Hill, New York, 1962, ch. 17. ¹¹ C. H. Rochester. Trans. Faraday Soc., 1963, **59**, 2820, 2826.