Primary Hydrogen–Deuterium Kinetic Isotope Effects in the Reduction of Triarylcarbonium Ions by Formate Anion

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The rates of reduction of 16 triarylcarbonium ions to the corresponding triarylmethanes by HCO_2Na and DCO_2Na have been measured in 71.0% aqueous trifluoroacetic acid containing 2.50M-formate. Brønsted plots of log k_H and log k_D against pK_{R^+} of the carbonium ion are slightly curved with the curvature of the former being the more pronounced. The kinetic isotope effect k_H/k_D varies between 1.8 and 3.2 and shows a maximum near pK_{R^+} of −4, the first such maximum observed for a hydride transfer process.

CONSIDERATION of the various vibrational modes of the activated complex led Westheimer [1] to suggest that the primary isotope effects in hydrogen-transfer reactions would be a maximum when the hydrogen is half-transferred, the magnitude of the isotope effect decreasing as the transition state deviates from the symmetrical case. Thus in such reactions the primary isotope effect should be a useful guide to transition-state structure.[2] Bell has shown [3] that such a maximum can arise from quantum mechanical tunnelling, and recently Kresge has demonstrated [4] that Marcus rate theory [5] predicts such a maximum (though in the latter case, the maximum need not necessarily occur exactly at the point of half-transfer).

Much effort has been expended in testing this hypothesis, and such a maximum has been clearly demonstrated for proton transfers from carbon acids,[3,4,6] and less clearly for base-catalysed elimination reactions.[7,8] Also many systems have been shown to exhibit an isotope effect that varies systematically with the overall energy change of the reaction.[9]

We now report such a maximum for a system involving a hydride transfer, the reduction of triarylcarbonium ions by formate anion [equation (1)].

$$Ar_3C^+ + HCO_2^- \longrightarrow Ar_3CH + CO_2 \qquad (1)$$

Hydride transfers have largely been ignored in the search for what has been called a 'Westheimer maximum',[7] possibly because isotope effects in hydride transfers are generally believed to be small (though this is not always the case [10]), or because of uncertainty regarding the geometry of the transition state in such transfers.[11] The reduction of the trityl cation by formate anion was established as a hydride transfer by Stewart,[12] and subsequently investigated further by Grinter and Mason,[13] who showed that a Brønsted plot for the reduction of a series of phenyl-substituted triphenylcarbonium ions with formate anion had a slope of 0.54, indicating that the hydride is approximately half-transferred in the transition state. In suggesting this, Grinter and Mason made the assumption that the equilibrium between carbonium ion and carbinol is a good model, in a relative sense, for the equilibrium between carbonium ion and the corresponding methane. This assumption has been made by other authors,[14] and seems justified in the light of the limited evidence available, so long as the system being examined does not alter fundamentally. For example, in the reduction of benzoic acid to toluene, the overall enthalpy change (calculated from heat of formation [15]) varies in the following way with substitution: unsubstituted, 398; *p*-methyl, 401; *m*-methyl, 400; *p*-fluoro, 399; *m*-iodo, 396; *p*-iodo, 383; *p*-nitro, 392 kJ mol^{-1}; On the other hand, the overall enthalpy change varies markedly in the series triphenylmethanol–triphenylmethane ($\Delta\Delta H_f$ 165; diphenylmethanol–diphenylmethane 194; and benzyl alcohol–toluene 173 kJ mol^{-1}).

EXPERIMENTAL

Reagents.—Most of the triarylmethanols and triarylmethanes examined were known compounds. Many were available from laboratory stock, and others were prepared by standard methods. α-Deuteriotriarylmethanes were prepared by the reduction of the corresponding carbonium ion perchlorate with lithium aluminium deuteride.[16] All compounds were either recrystallised or distilled prior to use.

4-Bromo-4′,4″-dimethyltriphenylmethanol was prepared by the reaction between *p*-tolylmagnesium bromide and ethyl *p*-bromobenzoate. Work-up yielded a dark yellow oil, which crystallised from aqueous ethanol (90%) as a

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[1] F. H. Westheimer, *Chem. Rev.*, 1961, **61**, 265.

[2] M. M. Kreevoy in 'Isotopes in Organic Chemistry', eds. E. Buncel and C. C. Lee, Elsevier, Amsterdam, 1976, vol. 2.

[3] R. P. Bell, 'The Proton in Chemistry', Cornell University Press, New York, 1973, 2nd. edn., p. 278.

[4] A. J. Kresge, D. S. Sagatys, and H. L. Chen. *J. Amer. Chem. Soc.*, 1977, **99**, 7228.

[5] R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 891.

[6] F. G. Bordwell and W. J. Boyle, *J. Amer. Chem. Soc.*, 1971, **93**, 512.

[7] L. F. Blackwell, *J.C.S. Perkin II*, 1976, 488.

[8] P. J. Smith in ref. 2.

[9] R. A. More O'Ferrall, in 'Proton Transfer Reactions,' eds. E. F. Caldin and V. Gold, Chapman and Hall, London, 1975, p. 201.

[10] R. Stewart, in ref. 2.

[11] R. A. More O'Ferrall, *J. Chem. Soc.* (*B*), 1970, 785.

[12] R. Stewart, *Canad. J. Chem.*, 1957, **35**, 766.

[13] R. Grinter and S. F. Mason, *Trans. Faraday Soc.*, 1964, **60**, 889.

[14] R. A. Breslow and W. Chu, *J. Amer. Chem. Soc.*, 1973, **95**, 411.

[15] (*a*) J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds,' Academic Press, London and, New York, 1970. (*b*) R. A. Keller, 'Basic Tables in Chemistry,' McGraw-Hill, New York, 1967.

[16] L. M. McDonough, Ph.D. Thesis, University of Washington, 1961.

yellow solid. Recrystallisation from ethanol (twice) gave needles (9%), m.p. 105.5—106° (Found: C, 69.8; H, 5.8; Br, 20.5. Calc. for $C_{21}H_{19}BrO$: C, 68.7; H, 5.2; Br, 21.8%). It was found to be impossible to obtain an entirely satisfactory analysis for this compound. Analyses were non-reproducible, the percentages of hydrogen and carbon increasing, and that of bromine decreasing, with time. For this reason measurements were made on as fresh a sample as possible. Other workers[17] have had difficulty obtaining good analyses of similar compounds.

4-*Methoxy-4′-methyltriphenylmethanol* was prepared by the reaction of *p*-tolylmagnesium bromide with 4-methoxybenzophenone. Work-up yielded a yellow oil which resisted crystallisation. The pure compound was separated as a clear, viscous liquid in 15% yield by chromatography on a 9 in silica column using 8% diethyl ether in light petroleum (b.p. 30—60°) as eluant, b.p. 230—234° at 0.3 mmHg (Found: C, 82.5; H, 6.9. $C_{21}H_{20}O_2$ requires C, 82.9; H, 6.6%).

4,4′-*Dimethoxy*-4″-*trifluoromethyltriphenylmethanol* was prepared by the reaction of *p*-methoxyphenylmagnesium bromide with ethyl *p*-trifluoromethylbenzoate. Work-up yielded a yellow oil which resisted crystallisation. The pure compound was obtained in 12% yield as a viscous, yellow liquid by chromatography on a 9 in silica column using 15% diethyl ether in light petroleum (b.p. 30—60°) as eluant, b.p. 206—208 at 0.3 mmHg (Found: C, 68.0; H, 5.1; F, 14.6. $C_{22}H_{19}F_3O_3$ requires C, 68.0; H, 4.95; F, 14.7%).

Trifluoroacetic acid was doubly distilled prior to use. Sodium formate was crystallised from methanol–water (70 : 30) before use. The deuterium content in the sodium [^{2}H]formate (claimed by Merck, Sharpe, and Dohme Isotopes to be at least 99%) was checked in two ways. First the ^{1}H n.m.r. spectrum of accurately measured 50 : 1 sodium [^{2}H]formate–sodium acetate in deuterium oxide was taken, and the protium content of the sodium formate determined from the integration to be $<1\%$. Secondly, an excess of triphenylmethanol was added to a solution of sodium[^{2}H]formate in 71% aqueous trifluoroacetic acid, and the solution refluxed until the yellow colour virtually disappeared (12 h). The triphenyl[^{2}H]methane produced was extracted and purified, and the ^{1}H n.m.r. spectrum of a measured quantity of this along with a measured quantity of iodoform taken in $CDCl_3$: examination of the integrals of the relevant peaks showed the protium content of the triphenylmethane to be at most 0.9%. Measurements were made on successive batches of sodium [^{2}H]formate, and all were found to contain $<1\%$ ^{1}H.

Measurements.—(a) *Formate reductions*. Reaction conditions were chosen so as to minimise the protonation of added formate anion while retaining sufficiently high acidity to keep a wide range of carbonium ions available for study. The conditions chosen were 2.50M-sodium formate in 8.50M (71.0%) aqueous trifluoroacetic acid. Such a solution was found to have a H_R value of -5.70, for both added HCO_2Na and DCO_2Na. (H_R in the absence of sodium formate is -6.4.[18])

Triarylmethanols were dissolved in 100% trifluoroacetic acid and this solution (0.03 cm^3) was added to the solution (10 cm^3) described above, to give an optical density of *ca.* 0.5. The flasks containing the resulting solutions were wrapped in aluminium foil and kept almost totally immersed in a water-bath thermostatted at 25.0 (±0.1°). Optical densities at the maximum absorption were measured regularly, using 1 cm cells, on a Cary 16 spectrophotometer.

Since the reactions were generally slow, the rates of the acid-catalysed decompositions of the carbonium ions were also measured in a 65.5% aqueous trifluoroacetic acid solution, containing no added formate. This solution has the same H_R value[18] as the kinetic solutions. The rate constants so obtained were used to correct the rates obtained in the formate reduction for acid-catalysed decomposition.

The reactions followed pseudo-first-order kinetics, and rate constants were evaluated directly from plots of log (optical density) *versus* time. In the case of the less basic alcohols it was necessary to correct for partial ionisation of the alcohol.[12] Most reactions were followed to between 25 and 50% completion, but some were followed for longer periods to demonstrate that pseudo-first-order kinetics prevailed to $>90\%$ completion.

Rate constants obtained in this manner were found to be reproducible to within 5%, and within experimental error of those obtained by simply measuring a fresh solution, sealing it in a tube, and immersing totally in a water-bath for a set time, before retrieving and remeasuring.

In all these reactions a rapid, initial reaction consumes a small quantity of carbonium ion before the slower, formate reduction may be observed. (This phenomenon has previously been observed in formic [^{2}H]acid.[12]) It was found that the quantity of carbonium ion consumed was independent of its concentration, but directly proportional to the concentration of added formate. It appears that commercial sodium formate contains a very small quantity of a highly reactive impurity, which cannot be removed by crystallisation. This initial reaction was therefore ignored in kinetic calculations.

(b) *Oxidation of triarylmethanes*. Solutions of triarylmethanes (usually *ca.* 5.0×10^{-4} mol) were prepared by dissolving the required quantity of compound in glacial acetic acid, then adding 0.050 0 cm^3 of this solution to 71% aqueous trifluoroacetic acid (10.00 cm^3). (Acid solutions were opened to the air at 25° for 24 h prior to addition to ensure that the oxygen content of the solution was at equilibrium with the air.) Reaction was monitored by following the appearance of the carbonium ion.

(c) pK_{R^+} *Values*. The pK_{R^+} values of many of the alcohols have already been measured in trifluoroacetic acid.[18] Others were measured in the usual way, using H_R values available for this medium,[18] and using the method of Johnson *et al.*[19] to compensate for medium effects when these arose. Table 1 lists pK_{R^+} values for the alcohols examined, and their spectral properties.

Temperature Effect.—Since the reaction appeared to be very sensitive to temperature, it was decided to follow the rate of reaction of one, virtually completely ionised alcohol, as it varied with temperature. The rate of reaction of 4,4′-dimethyltriphenylmethanol was measured at 35 and 45°, as well as at 25°. A plot of $\ln(k/T)$ *versus* $1/T$ (where k is the pseudo-first-order rate constant) was accurately linear (r 1.000) and indicated an enthalpy of activation of 113 kJ mol^{-1}. This must be regarded as an ' apparent ' heat of activation, since a change in temperature will change the acidity of the system (hence the quantity of carbonium ion

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[17] A. G. Evans, J. A. G. Jones, and G. O Osborne, *Trans. Faraday Soc.*, 1954, **50**, 16, 470.

[18] U. A. Spitzer, T. W. Toone, and R. Stewart, *Canad. J. Chem.*, 1976, **54**, 440.

[19] C. D. Johnson, A. R. Katritzky, B. J. Ridgewell, N. Shakir, and A. M. White, *Tetrahedron*, 1975, **21**, 1055.

and unprotonated formate anion) as well as changing the rate of reaction of the two species.

TABLE 1

$\mathrm{p}K_{\mathrm{R}^+}$ Values and spectral properties of triarylmethanols

Compound no.	Substituted triphenylmethanol	$-\mathrm{p}K_{\mathrm{R}^+}$	$\lambda_{\mathrm{max.}}$nm	log ε [e]
(1)	4-Methoxy-4′-methyl	2.25	473	4.73
(2)	4,4′-Dimethoxy-4″-trifluoromethyl	2.34	509	4.96
(3)	4,4′,4″-Trimethyl [a]	2.81	446	4.97
(4)	4-Methoxy [a]	3.18	469	4.82
(5)	4,4′Dimethyl [a]	3.78	451	4.81
(6)	4-Bromo-4′,4″-dimethyl	4.26	455	4.97
(7)	4,4′4″-Triphenyl [b]	4.35	543	4.92
(8)	3,3′,3″-Trimethyl	4.78	410	4.61
(9)	4-Methyl [a]	4.81	450	4.70
(10)	2-Methyl	5.19	424	4.74
(11)	4-Phenyl	5.35	504	4.75
(12)	4-Fluoro [c]	6.42	427	4.70
(13)	Unsubstituted [a]	6.44	425	4.60
(14)	3-Methoxy [d]	6.74	418	4.61
(15)	4-Methyl-3′-trifluoromethyl	6.88	451	4.70
(16)	4-Chloro	7.00	442	4.73
(17)	4-Bromo	7.15	453	4.74
(18)	4,4′-Dichloro	7.63	453	4.89
(19)	3-Chloro [d]	7.81	411	4.66

[a] Data from ref. 18. [b] Plots of log (ionisation ratio) *versus* H_{R} for this compound showed distinct curvature, the slope increasing with increasing acidity. The $\mathrm{p}K_{\mathrm{R}^+}$ value used is that measured in formic acid.[13] Fortuitously the measured degree of ionisation in aqueous trifluoroacetic acid at H_{R} −5.70 is the same as that calculated from the equation $\log I = \mathrm{p}K_{\mathrm{R}^+} + 5.70$ using the $\mathrm{p}K_{\mathrm{R}^+}$ measured in formic acid, and so little error is introduced into the rate constant when correcting for the degree of ionisation. [c] The absorbance of this compound in acid showed a marked increase with time, an effect caused by the appearance of a large peak at λ 464 nm. A preparative study involving refluxing this compound in 65.5% aqueous trifluoroacetic acid for 3 h yielded 4-hydroxytriphenylmethanol (as its dehydrated form) in high yield showing the fluorine to be fairly rapidly replaced in a nucleophilic attack by water in this medium. [d] Decomposes too quickly for kinetic study. [e] In 100% trifluoroacetic acid.

Preparative Reduction.—The system of sodium formate in trifluoroacetic acid was examined to test its efficacy in reducing a variety of substrates. The system proved unable to reduce 4,4′-dichlorobenzophenone or 9-phenylfluoren-9-ol, but was highly efficient in reducing more basic substrates such as triphenylmethanol. This compound (0.52 g) was reduced to triphenylmethane in 73% yield after 20 min reflux in a 2.5M solution of sodium formate in 71% aqueous trifluoroacetic acid (100 cm^3). The yield was increased to 83% when reflux was extended to 60 min. Under similar conditions 4-chlorotriphenylmethanol was reduced to the corresponding methane in 82% yield after 4 h reflux.

TABLE 2

Rate constants and primary isotope effects for the oxidation of triarylmethanes

Substituted triphenylmethane	k_{H}, pseudo-first-order rate constant for oxidation of ^{1}H compound (min^{-1})	k_{D}, pseudo-first-order rate constant for oxidation of ^{2}H compound (min^{-1})	Primary isotope effect
4,4′,4″-Trimethoxy	2.26×10^{-6}	1.28×10^{-6}	1.7
4,4″-Dimethoxy	6.14×10^{-7}	2.23×10^{-7}	2.8
4,4′,4″-Trimethyl	(2.23×10^{-7})	(1.51×10^{-7})	(1.5)
4,-Methoxy	1.02×10^{-7}	2.34×10^{-8}	4.4
Unsubstituted	(6.4×10^{-9})	(9.6×10^{-9})	

Alcohols that give more stable carbonium ions required a longer reaction time. Tris-4-methylphenylmethanol was reduced to the corresponding methane in 57% yield after 23 h reflux; 4-methoxytriphenylmethanol required 48 h reflux to produce 40% of the corresponding methane.

4-Methyltriphenylmethanol (0.37 g) was refluxed for 60 min in a solution of 2.5M-sodium [^{2}H]formate in 71% aqueous trifluoroacetic acid (17 cm^3) and gave an 80% yield of 4-methyltriphenylmethane. Analysis of the ^{1}H n.m.r. spectrum of the product in $CDCl_3$ containing a measured amount of iodoform showed 97.5% deuterium incorporation in the methane.

In another experiment triphenylmethanol was reduced in 71% aqueous trifluoroacetic acid containing equimolar HCO_2Na–DCO_2Na. Analysis of the ^{1}H n.m.r. spectrum of the triphenylmethane produced revealed 31.3% deuterium incorporation, indicating an isotope effect of 2.2, in reasonable agreement with the kinetic data. (The value of 2.1 obtained at 25° may be expected to be lowered[10] to 1.8 at 90°, the temperature of the preparative reduction.)

RESULTS AND DISCUSSION

Oxidation of Triarylmethanes.—During the course of this work it was observed that some triarylmethanes are oxidised in trifluoroacetic acid solution to the corresponding carbonium ions. This phenomenon has previously been observed in sulphuric and polyphosphoric acids.[20] If this oxidation were subject to a large isotope effect it could lower the observed isotope effect for the formate reduction, and so it was examined further.

Several triarylmethanes were investigated, and pseudo-first-order rate constants for the oxidations are presented in Table 2. Only very approximate values could be obtained for unsubstituted triphenylmethane, as it reacts very slowly. 4,4′-Dinitrotriphenyl[^{1}H]methane was also investigated, but showed no reaction after more than one month. (In the latter case it was necessary to use a sampling technique, since the carbonium ion would be entirely converted into the alcohol in 71% aqueous trifluoroacetic acid. At regular intervals 1 cm^3 portions of the solution were diluted to 10 cm^3 with concentrated sulphuric acid and the visible spectrum recorded. The resulting solution would be sufficiently acidic to ionise any 4,4′-dinitrotriphenylmethanol present.)

After a variable initiation period (usually about two days), during which carbonium ion was generated very slowly, the rate increased markedly and then achieved a steady state. (In most reactions only a small percentage of the reaction could be followed. Some compounds, however, were investigated at lower concentrations of triarylmethane, and the reaction shown to be pseudo-first order up to 12% completion).

For the methoxy-substituted triphenylmethanes rate constants were reproducible within a few percent. In the case of the tri-*p*-tolylmethane however, rate constants were difficult to reproduce, a fact possibly connected with the apparent tendency of this compound to sublime from solution (and turn an intense yellow in the ground glass joint at the top of the flask).

From the data on the methoxy-substituted triphenylmethanes it is possible to see that the rate of oxidation decreases as the carbonium ion produced becomes less thermodynamically stable. In fact a plot of log k_H *versus* pK_{R^+} is linear with a slope of 0.425 (r 1.000).

Experiments at approximately the concentrations used in the formate-reduction kinetics, while giving similar rate constants to those evaluated for more concentrated solutions, indicated that the generation of carbonium ion from triarylmethanes was unlikely to have any effect on rate constants (or isotope effects) evaluated in the formate reduction of the triarylcarbonium investigated in this study.

TABLE 3

Rate constants and primary isotope effects for the formate reduction of triarylcarbonium ions in 71.0% aqueous trifluoroacetic acid at 25°

Compound [a]	Pseudo-first-order rate constant for protium transfer $10^6\ k_H/\text{min}^{-1}$ [b]	Pseudo-first-order rate constant for deuterium transfer $10^6\ k_D/\text{min}^{-1}$	Primary isotope effect k_H/k_D [c]
(1)	0.304 ± 0.012(3)	0.143 ± 0.009(3)	2.1 ± 0.2
(2)	0.197 ± 0.008(3)	0.107 ± 0.024(3)	1.8 ± 0.4
(3)	0.926 ± 0.087(3)	0.369 ± 0.009(3)	2.5 ± 0.2
(4)	0.782 ± 0.042(4)	0.247 ± 0.013(3)	3.2 ± 0.2
(5)	3.61 ± 0.18(4)	1.22 ± 0.04(4)	3.0 ± 0.2
(6)	5.78 ± 0.15(3)	1.80 ± 0.12(3)	3.2 ± 0.2
(7)	5.31 ± 0.04(3)	1.78 ± 0.11(3)	3.0 ± 0.2
(8)	14.1 ± 0.85(3)	6.15 ± 0.23(3)	2.3 ± 0.2
(9)	12.1 ± 1.50(3)	4.65 ± 0.28(3)	2.6 ± 0.4
(10)	23.6 ± 2.49(3)	7.45 ± 0.86(3)	3.2 ± 0.5
(11)	12.2 ± 0.2(3)	4.96 ± 0.21(3)	2.5 ± 0.1
(13)	50.7 ± 3.1(4)	23.8 ± 0.8(4)	2.1 ± 0.1
(15)	56.3 ± 1.8(3)	31.3 ± 0.7(2)	1.8 ± 0.1
(16)	71.2 ± 0.4(3)	28.9 ± 1.7(3)	2.5 ± 0.1
(17)	74.1 ± 3.3(3)	36.8 ± 1.8(3)	2.0 ± 0.1
(18)	72.3 ± 5.1(2)	40.2 ± 2.1(2)	1.8 ± 0.2

[a] Numbering as in Table 1. [b] Quoted error is the standard deviation of several (number in parentheses) determinations. [c] Quoted error is calculated from the standard deviations in k_H and k_D by standard procedures (See J. Topping, ' Errors of Observation and Their Treatment ,' Chapman and Hall, London, 1962, 3rd edn. p. 82.).

It was found that degassing the solutions very care fully (and keeping them free of oxygen) reduced the rate of generation of carbonium ion. In fact, carbonium ion was generated at the same rate as that observed in the initiation period {in the case of tris-4-methoxyphenyl-[^{1}H]methane, k_H (degassed) = 1.27×10^{-7} min^{-1}}, and no dramatic increase in rate was observed. The effect was almost identical to that of adding hydroquinone (1.0×10^{-4}M) to the solution {k_H (added hydroquinine) = 1.58×10^{-7} min^{-1} for tris-4-methoxyphenyl[^{1}H]methane}.

It appears that the generation of carbonium ion from triarylmethanes in these solutions occurs by two pathways. The faster is a radical process that involves oxygen and requires an initiation period; the slower does not appear to involve either radicals or molecular oxygen. It is interesting that Deno *et al.*[20] observed that the analogous process in polyphosphoric acid may be stopped by degassing and keeping the solution in the dark, whereas this does not stop the oxidation in sulphuric acid.

Formate Reduction of Triarylcarbonium Ions.—Rate data for the formate (^{1}H and ^{2}H) reduction of various triarylcarbonium ions are presented in Table **3**, in which k_H and k_D (the pseudo-first-order rate constants for reduction by [^{1}H]- and [^{2}H]-formate, respectively) are corrected for partial ionisation of the alcohol and acid-catalysed decomposition of the carbonium ions. Table **3** includes data on 2-methyltriphenylmethanol [compound (10)], but since steric factors could be important in the reactions of this compound, it is omitted in subsequent discussion.

The rate constants for compounds (1)—(3) include one run in which the solutions were degassed and sealed in cells under a helium atmosphere. [The cells were then thermostatted at 25.0 (±0.1)° for the duration of the experiment.] Although our studies (see above) on the oxidation of triarylmethanes indicated that the oxidation would not interfere significantly with our results, in view of the importance of these three compounds to our findings, and as these three are the most likely affected by oxidation, this was a necessary precaution. It was found that the degassed solutions gave rate constants within experimental error of those solutions which were not degassed.

Figure 1(a) shows a plot of log k_H *versus* pK_{R^+}. The best (least-squares fit) straight line through the data has a slope of 0.473 (r 0.973). Figure 1(b) shows a plot of log k_D *versus* pK_{R^+}, for which the best straight line has a slope of 0.491 (r 0.983). However, both plots show distinct curvature, the curvature being greater for the protio plot. Least squares analysis fitting the best quadratic equation to the data gives the curves represented by equations (2) and (3). [The respective curves are drawn as dotted lines in Figures 1(a) and (b).] The curvature is in the same direction found for proton

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[20] N. C. Deno, G. Saines, and M. Spangler, *J. Amer. Chem. Soc.*, 1962, **84**, 3295.

transfers,[3,21] and the origins of such an effect have received much attention in the literature.[3,22] The greater

$$\log k_{\mathrm{H}} = -0.063\,0\ \mathrm{p}K_{\mathrm{R^+}}{}^2 - 1.093\,1\ \mathrm{p}K_{\mathrm{R^+}} - 8.765\,9 \quad (2)$$

$$\log k_{\mathrm{D}} = -0.041\,7\ \mathrm{p}K_{\mathrm{R^+}}{}^2 - 0.902\,1\ \mathrm{p}K_{\mathrm{R^+}} - 8.778\,3 \quad (3)$$

curvature ot the protio reaction could conceivably be a consequence of tunnelling.

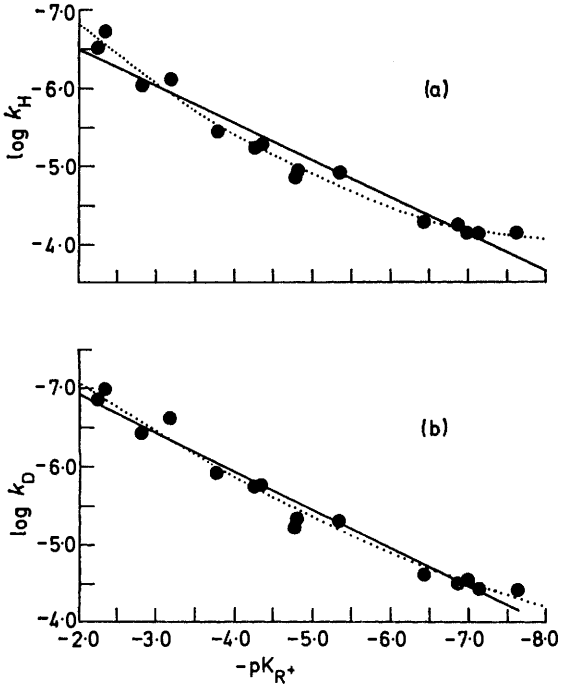

FIGURE 1 Brønsted plots for (a) [^{1}H]formate and (b) [^{2}H]formate reduction of triarylcarbonium ions. (Full line is best straight line, and dotted line is best quadratic curve, fitted by the method of least squares)

Figure 2 shows a plot of the primary isotope effect *versus* p$K_{\mathrm{R^+}}$. Least squares analysis gives the best fitting quadratic equation as (4) and the curve shows a

$$k_{\mathrm{H}}k_{\mathrm{D}} = 0.119\,9pK_{\mathrm{R^+}}{}^2 - 1.080\,4\ \mathrm{p}K_{\mathrm{R^+}} + 0.378\,9 \quad (4)$$

distinct maximum in the region of p$K_{\mathrm{R^+}}$ −4.51. This is the first isotope effect maximum observed for a hydride transfer reaction.

It is noteworthy that the most obvious deviations from the smooth curve arise for compounds (8) and (9), and that the slightly reduced isotope effects in these cases arise from the rate of the deuterio reaction being slightly faster than expected. This effect is real, and does not arise from isotopic impurity in a particular batch of sodium [^{2}H]formate; the rates were reproducible with different batches of sodium [^{2}H]formate, and other compounds measured with the same batches of sodium [^{2}H]formate showed no such enhancement of rate. Further, a preparative reduction (see Experimental section) of one of these compounds showed 97.5% deuterium incorporation.

Olah and Svoboda[23] have argued that reduction of arylmethyl cations by hydride donors takes place by initial attack of a lone pair donor (formate ion in our case) on the *ortho* (or *para*) position of one of the aryl rings to form a σ-complex which subsequently breaks down, hydrogen being transferred to the aliphatic centre in the process. This mechanism could conceivably account for the pronounced drop-off in isotope effect observed for the three least reactive carbonium ions (left hand side of Figure 2) if σ-complex formation were becoming partially rate determining in these cases. Since the Brønsted plots do not show a break at this point we prefer, in the absence of other evidence, to regard the reactions as simple hydride transfers.

The magnitude of the isotope effect deserves comment. Most, but certainly not all, reactions that can be confidently designated hydride transfers have rather modest isotope effects; many are in the range 3—5[10] at room temperature, which is smaller than that calculated from the difference in zero-point stretching levels. Although some extremely large isotope effects have been observed in proton and hydrogen-atom transfer processes,[24] many others fall in the range of 3—5 and diagnosing mechanism on the basis of the magnitude of the isotope effect is extremely risky. Nonetheless, the range of isotope effect we observe, 1.8—3.2 at 25°, tends to reinforce the notion that the isotope effect associated with hydride transfer is likely to be small.[25]

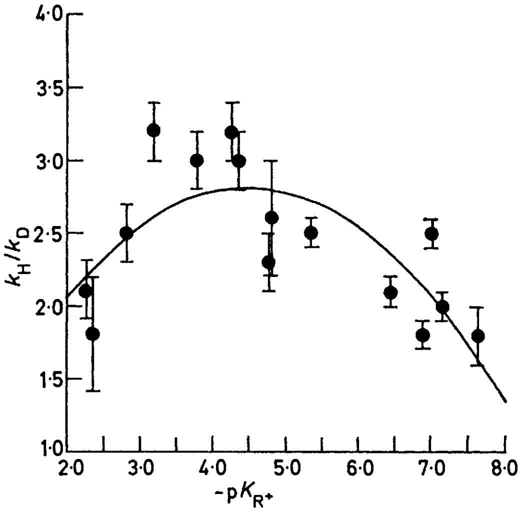

FIGURE 2 Primary isotope effect for formate reductions *versus* p$K_{\mathrm{R^+}}$ of triarylcarbonium ions

What is the significance of the H_{R} value at the isotope-effect maximum? The demonstration that triarylmethanes containing electron-donating groups slowly

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[21] M. Eigen, *Angew. Chem. Internat. Edn.*, 1964, **3**, 1.

[22] (*a*) A. J. Kresge, *Accounts Chem. Res.*, 1975, **8**, 354; (*b*) E. Buncel and H. Wilson, *Adv. Phys. Org. Chem.*, 1977, **14**, 133.

[23] G. A. Olah and J. J. Svoboda, *J. Amer. Chem. Soc.*, 1973, **95**, 794.

[24] See, for example, E. F. Caldin and S. Mateo, *J.C.S. Chem. Comm.*, 1973, 854; G. Brunton, D. Griller, L. R. C. Barclay, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1976, **98**, 6803.

[25] E. S. Lewis and M. C. R. Symons, *Quart. Rev.* 1958, **12**, 230.

generate carbonium ion, even in the apparent absence of molecular oxygen, suggests that the conversion of carbonium ion to alkane is reversible and raises the question of whether the maximum coincides with the position where the overall free energy change is zero, a situation that occurs with a number of proton transfers. Since even the least reactive carbonium ions show no departure from strict first-order kinetics over the reaction range studied, we conclude that the isotope-effect maximum is well removed from the position of zero free energy change.

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