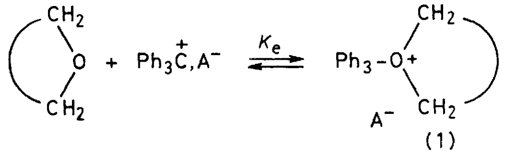
Hydride Ion Transfer between Triphenylmethyl Cation and Tetrahydrofuran, 1,3-Dioxolan, and 1,3-Dioxepan

By **Kabir-ud-Din** † and **Peter H. Plesch,*** Chemistry Department, The University, Keele, Staffordshire ST5 5BG

A polarographic study of the rates of hydride ion transfer from tetrahydrofuran, 1,3-dioxolan, and 1,3-dioxepan to the triphenylmethyl cation has provided data for comparing the effects of ring structure and size and of polarity of solvents on this reaction. The results are compared with those obtained by other authors with the same and with related compounds by spectroscopic methods. The reaction is insensitive to ionic strength and only slightly affected by polarity of solvent. The cyclic carboxonium ions which are the other reaction products, are too stable to be detected polarographically.

IN the course of our studies on the polarography of organic cations we wished to find out whether carboxonium ions with a delocalised charge could be identified polarographically. The easiest way of forming these ions is by reaction of a trityl salt with a cyclic ether or a 1,3-dioxacycloalkane.[1] This reaction has been studied extensively in the context of the initiation of the polymerisation of tetrahydrofuran (THF) [2] and of 1,3-dioxolan (DXL) [3] by trityl salts. It was found that the formation of the tertiary oxonium ion (1) by reaction (1) is unimportant in many systems, and that in these the hydride abstraction (2) is dominant; the carboxonium ions (2) formed thus are the species which we wanted to study. The formation of triphenylmethane has been shown for cyclic ethers [2] and for 1,3-dioxacycloalkanes.[3] It turned out that the ions (2) are not reducible in the potential range accessible in this work. However we could determine the kinetics of the reaction (2) for THF, DXL, and 1,3-dioxepan (DXP) in methylene chloride by monitoring the concentration of the trityl ion polarographically.[4] All the previous kinetic work on this reaction had been done spectroscopically.[2d, 3c, 5, 6]



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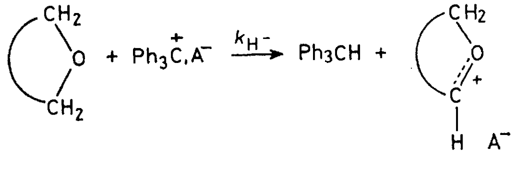

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EXPERIMENTAL

Materials.—1,3-Dioxolan and 1,3-dioxepan were prepared conventionally. Tetrahydrofuran was a commercial product (May and Baker). Purification and handling procedures of these materials and also of the solvent methylene chloride have been described in detail.[7] Trityl tetrafluoroborate was prepared entirely under vacuum from trityl chloride and silver tetrafluoroborate.[8] The product, dissolved in methylene chloride, was distributed into weighed phials.[9] The concentration of trityl salt solutions was determined spectrophotometrically. Tetra-n-butylammonium tetrafluoroborate (TBAFB) and tetra-n-butylammonium perchlorate (TBAP) were prepared and purified as described.[10]

Apparatus.—A Beckman Electroscan 30 instrument was used for recording the polarograms. The polarographic vessel and the electrodes were as described,[4, 10] with the following modifications. The anode was a long coiled Pt wire, and for reference we used the electrode: Ag/0.5M-TBAP in CH_2Cl_2, AgI(sat.), $Bu^n{}_4N^+Ag_3I_4^-$(sat.) with a connecting side arm containing 0.5M-TBAP solution in CH_2Cl_2. The potential of the reference electrode was -0.141 ± 0.003 V *vs.* the S.C.E. All potentials are given with respect to our reference electrode. A dropping mercury electrode with $t = 2.77$ s, $m = 2.60$ mg s^{-1} at $h = 35.5$ cm in 0.1M-TBAFB/CH_2Cl_2 (open circuit) was the working electrode.

Procedure.—The procedure and manipulations under high vacuum were the same as used earlier.[4, 10] After evacuating the vessel containing the supporting electrolyte (TBAFB) and a phial of trityl salt solution, a small portion of the freshly distilled solvent was run into it and then the phial was broken. After the required amount of the solvent had been added, the reference and working electrodes were inserted through appropriate ground-glass joints against a nitrogen stream. A polarogram for reduction of the trityl ion was recorded. Then the required amount of the hydride ion donor was added as a solution in CH_2Cl_2 from a burette which had been previously filled under vacuum, and then the polarograms were recorded at different times. The experiments were performed at ambient temperature.

RESULTS AND DISCUSSION

The polarograms taken at increasing times showed only one wave which, as reported previously,[4] was the revers-

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† On leave from Aligarh Muslim University, Aligarh, India.

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ible one-electron wave for the trityl ion reduction, with $E_{\frac{1}{2}}$ *ca.* 0.51 V, whose height i_d decreased with time. Since good first-order plots were obtained for this decrease over more than two half-lives, all the reactions were internally of first order:

$$-\mathrm{d}[Ph_3C^+]/\mathrm{d}t = k_1[Ph_3C^+]$$

The results of Penczek [3c] indicate that reaction (2) is also of first order with respect to the hydride donor RH, so that $k_1 = k_{H^-}[RH]$. Since in all our experiments $[RH]_0 \gg [Ph_3C^+]$, we could calculate k_{H^-} from the relation $k_{H^-} = k_1/[RH]_0$. Our values of k_{H^-}, together with some reported by others, are given in the Table.

The fact that we found only one wave in all systems indicates that the concentration of the tertiary oxonium ions (1) must have been too small for polarographic detection under our conditions. The earlier results of Plesch and Thomas [10] as well as our own [11] indicate that such ions would have been reduced in the potential range over which we worked (0.92 to −1.50 V). The very low concentration of tertiary oxonium ions in our systems agrees with Penczek's conclusion about the low concentrations of ions of type (1) in his systems. This comparison is valid, despite the high ionic strength in our systems, as the equilibria of type (1) are not generally very sensitive to ionic strength.

Rate-constants for the hydride ion abstraction by trityl cation, with 0.1M-TBAFB as supporting electrolyte

$10^3[Ph_3C^+]$/ mol dm^{-3}	RH	$10^3[RH]$/ mol dm^{-3}	Solvent	ε (at 25 °C)	$10^3k_{H^-}$/mol^{-1} dm^3 s^{-1}		Ref.
					This work	Lit.	
0.536	THF	14.034	CH_2Cl_2	8.93	3.90 ± 0.68 (*ca.* 18 °C)	6.3 (25 °C)	3*c*
0.273	DXL	15.169	CH_2Cl_2	8.93	7.76 ± 0.55 (*ca.* 22 °C)	12 (25 °C)	3*c*
0.384		8.779	CH_2Cl_2		9.72 ± 0.25 (*ca.* 22 °C)	7.71 (23 °C)	6
0.533		13.724	CH_2Cl_2		9.42 ± 0.13 (*ca.* 25 °C) [a,b]		
0.627	DXL	10.545	$(CH_2Cl)_2$	10.36	7.40 ± 0.04 (*ca.* 18 °C)		
0.551	DXP	77.082	CH_2Cl_2	8.93	2.66 ± 0.09 (*ca.* 22 °C)		
0.683		10.409	CH_2Cl_2		2.25 ± 0.11 (*ca.* 18 °C)		
1.017		45.704	CH_2Cl_2		2.41 ± 0.09 (*ca.* 22 °C)		
1.041		23.529	CH_2Cl_2		3.00 ± 0.05 (*ca.* 22 °C)		
0.476	DXP	7.906	$(CH_2Cl)_2$	10.36	1.42 ± 0.45 (*ca.* 18 °C)		

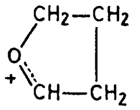
[a] In this experiment $Ph_3C^+PF_6^-$ and 0.1 mol dm^{-3} TBAP were used. [b] In 1974 Dr. F. G. Thomas obtained very similar k_{H^-} values with $Ph_3C^+SbF_6^-$ and 0.1 mol dm^{-3} TBAP in this laboratory.

In comparing our k_{H^-} for DXL with Penczek's and Jedlinski's values, we note a reasonable agreement, despite the fact that in their systems by far the greater fraction of the trityl ions were free, whereas in our experiments the most abundant species were ion-pairs and higher aggregates.

For THF a value of k_{H^-} at 25 °C can be obtained by extrapolating to 25 °C the low-temperature data of Table 4 of ref. 2*d*. The resultant (rather uncertain) $k_{H^-} = 2.7 \times 10^{-2}$ mol^{-1} dm^3 s^{-1} for the reaction in bulk THF (ε = 7.58) is ten times greater than ours for the more polar methylene chloride solvent. This is qualitatively as expected from transition state theory which predicts that a reaction between an ion and a molecule is accelerated by a reduction in the polarity of the medium. Our results with DXL and DXP provide a further opportunity to compare the rate-constants in two solvents, and for these too the less-polar solvent (methylene chloride) gives the greater k_{H^-}. The same effect has been found for two substituted dioxolans in methylene chloride and nitromethane.[6]

The fact that the rate-constant is less for DXP than for DXL may reflect the greater stability of the seven-membered ring, or the higher energy of the transition state leading to the formation of the seven-membered 2-ylium ion (4), or both.

The last point which needs comment is that we were unable to detect polarographically the ions (2) which we set out to find. The ion formed from THF has structure (3),[2c] that from DXL and DXP has structure (4).[1] Additional experiments with salts of (4) showed us that these ions cannot be reduced in the potential range accessible in methylene chloride, and it seems likely that



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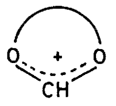

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the stability of (3) is also so great that its $E_{\frac{1}{2}}$ lies beyond the decomposition potential in our systems (−1.50 V at $i = 0.5$ μA).

We thank Dr. F. G. Thomas for advice and for permission to mention his unpublished results, Professor St. Penczek for helpful comments, and the S.R.C. for a Post-Doctoral research grant (to K.), and for technical assistance and equipment. One of us (K.) thanks the Aligarh Muslim University for leave of absence.

Note added in Proof. Electrochemical details of the electrodes, solvent, and base electrolytes used in this work have been given recently (Kabir-ud-Din and P. H. Plesch, *J. Electroanalyt. Chem.*, in the press).

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