

The Carbenium \rightleftharpoons Oxonium Ion Equilibrium. Part I. Reversible Reaction of Non-paired Triphenylmethyl Cation with Ethers and Acetals

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Equilibria between the non-paired triphenylmethyl cation and the corresponding oxonium ions, involving various linear and cyclic ethers and acetals, have been studied in CH_2Cl_2 over a wide temperature range. The standard enthalpy (ΔH_e°) and entropy (ΔS_e°) of equilibrium have been determined for twelve nucleophiles and it was found that ΔH_e° is a linear function of the basicity expressed as $\text{p}K_a$ or $\text{p}K_b$ (measured at 25°) of the corresponding nucleophile. The correlation factor is rather poor (0.7) and reflects the uncertainty of the basicity data. ΔH_e° and ΔS_e° change from $-5.8 \pm 0.2 \text{ kcal mol}^{-1}$ and $-24 \pm 1 \text{ cal mol}^{-1} \text{ K}^{-1}$ for 2-trichloromethyl-1,3-dioxolan to $-17 \pm 1 \text{ kcal mol}^{-1}$ and $-60 \pm 5 \text{ cal mol}^{-1} \text{ K}^{-1}$ for tetrahydropyran respectively. From a linear plot of ΔH_e° against ΔS_e° (correlation factor 0.97) the isoequilibrium temperature has been determined as 311 K.

In many chemical reactions the simultaneous existence of carbenium and oxonium ions at equilibrium is postulated, although this kind of equilibrium has never been thoroughly studied.

More than fifty years ago Hantzsch observed the diminution of intensity of the characteristic yellow colour of triphenylmethyl cation when ether was added to a solution of triphenylmethyl perchlorate.¹ This was attributed to the reversible formation of the ion from the colourless ester (perchlorate). Leffler later correctly proposed the formation of a colourless oxonium salt during the reaction as an explanation for the observed phenomenon² [reaction (1), $K_e = k_a/k_d$]. Smith and Rao

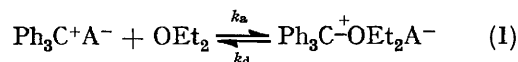
studied equilibrium (1) in acetic anhydride and nitromethane³ and attempted to determine the corresponding equilibrium constant K_e . In the former solvent self-consistent results (concentration of the oxonium ion formed was proportional to the product of the ether and triphenylmethyl cation concentrations) were obtained while in the latter erratic results were noted. This could be due either to the experimental conditions (semi-open system) or to the inherent reactivity of nitromethane towards triphenylmethyl cation.⁴ Recently, Brauman and Archie have studied an equilibrium similar to (1) in acetonitrile, but involving water

¹ A. Hantzsch, *Ber.*, 1921, **54**, 2573.

² I. E. Leffler, 'Reactive Intermediates in Organic Chemistry,' Interscience, New York, 1956, p. 97.

³ W. B. Smith and P. S. Rao, *J. Org. Chem.*, 1961, **26**, 254.

⁴ Y. Pocker, *J. Chem. Soc.*, 1958, 240.



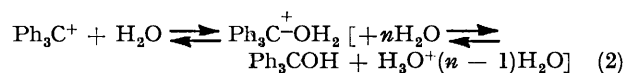
as a nucleophile, and using ^1H n.m.r. line broadening to determine the rate constants involved (k_a and k_d).⁵ The application of the n.m.r. method, which calls for the use of high concentrations of triphenylmethyl salt (10^{-1} – 10^{-2}M), complicated the quantitative treatment of the experimental data by the possible formation of ion pairs and their agglomerates.

Studies of the attack of nucleophiles on carbenium ions, and, especially, the determination of the absolute rate constants involved are important to understand factors governing the corresponding reactivities. For the most part, owing to the high reactivity of carbenium ions, direct measurements have been limited to relatively stable species such as highly substituted triphenylmethyl cations. Reaction rates of Crystal Violet,^{6,7} and *p*-methoxy- and other, more reactive triphenylmethyl cations have been studied, for both aqueous and (more rarely) nonaqueous systems.⁸ However, no study has been carried out for the unsubstituted triphenylmethyl cation.

In the present paper we describe the determination of the equilibrium constants (K_e) for the reversible interaction of triphenylmethyl cation with a number of linear and cyclic ethers and acetals in order to understand the influence of the structure of the nucleophile on the extent of 'onium ion formation. The conditions for these experiments have been chosen in such a way that the equilibria studied involved the non-paired (free from interaction with an anion) carbenium ion.

RESULTS

The reactions of triphenylmethyl cation with linear and cyclic ethers and acetals were studied in solutions of pure, dry methylene chloride. The extreme dryness of the solvent used is a necessary condition for obtaining reproducible values of the equilibrium constants K_e and the pertinent thermodynamic parameters. Water reacts with triphenylmethyl cation giving the corresponding protonated alcohol and/or hydronium ions with various degrees of solvation when there is an excess of water in a system [reaction (2)]. The water content in CH_2Cl_2 was deter-



mined by a method of our own based on equilibrium (2). This new method, allowing the determination of very low H_2O concentrations ($\leq 10^{-2}$ p.p.m.), is described in detail elsewhere.⁹

All measurements were performed in sealed apparatus with break-seals, the reagents being transported under vacuum (see Experimental section). Triphenylmethyl cation, in the form of the free (unpaired) ion, or contact or solvent separated ion pair, has the same spectrum, with two

⁵ J. I. Brauman and W. C. Archie, jun., *J. Amer. Chem. Soc.*, 1970, **92**, 5981.

⁶ E. F. J. Duynstee and E. Grunwald, *J. Amer. Chem. Soc.*, 1959, **81**, 4542.

⁷ V. C. Turgeon and V. K. LaMer, *J. Amer. Chem. Soc.*, 1952, **74**, 5988.

⁸ R. A. Diffenback, K. Sano, and R. W. Taft, *J. Amer. Chem. Soc.*, 1966, **88**, 4747; C. R. Ritchie, G. A. Skinner, and V. G. Badding, *ibid.*, 1967, **89**, 2063; E. A. Hill and W. J. Mueller, *Tetrahedron Letters*, 1968, 2565.

maxima at 413 and 435 nm. According to our measurements, properly purified triphenylmethyl salts with anions such as AsF_6^- , PF_6^- , SbCl_6^- , and SbF_6^- all give approximately the same molar extinction coefficient in CH_2Cl_2 solvent at 25°, e.g. ϵ_{max} (435 nm) = $3.95 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. Previous reports give ϵ_{max} ranging from 3.26×10^4 to $3.98 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$.¹³ The lower values were usually observed in organic solvents, while the high value was measured for triphenylmethanol in H_2SO_4 solution, and the lowering of the extinction coefficients has been attributed^{14,15} to unsatisfactory purification of solvents and resulting reversible and/or irreversible (e.g. solvolysis) reactions of the triphenylmethyl cation with adventitious nucleophiles. Our final test for the purity of CH_2Cl_2 consisted in placing ca. 10^{-5}M - Ph_3C^+ in the sealed apparatus and checking that no changes occurred in E_{435} at 25 and -78° . All these preliminary results are described in detail to stress the importance of the purity of the solvent.

The following ethers and acetals were employed in the study of the carbenium \rightleftharpoons oxonium ion equilibria: diethyl ether, dibutyl ether, tetrahydrofuran, tetrahydropyran, 1,4-dioxan, dimethoxymethane, diethoxymethane, 1,3-dioxolan, 1,3-dioxan, and 2-methyl-, 2-phenyl-, and 2-trichloromethyl-1,3-dioxolan. The concentration of triphenylmethyl cation $[\text{Ph}_3\text{C}^+]$ was determined according to relationship (3) where l is the optical path in cm. Knowing

$$[\text{Ph}_3\text{C}^+] = E_{435}/\epsilon_{435}l \quad (3)$$

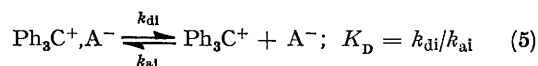
$[\text{Ph}_3\text{C}^+]$, measured before and after introduction of the ether or acetal under study ($[\text{Ph}_3\text{C}^+]_0$ and $[\text{Ph}_3\text{C}^+]$ respectively), the corresponding equilibrium constant K_e can be determined from equation (4) where $[\text{EA}]_0$ denotes

$$K_e = k_d/k_a = ([\text{Ph}_3\text{C}^+]_0 - [\text{Ph}_3\text{C}^+])/[\text{Ph}_3\text{C}^+] \cdot [\text{EA}]_0 \quad (4)$$

the starting concentration of the ether or acetal. In the majority of experiments $[\text{EA}]_0/[\text{Ph}_3\text{C}^+]_0 > 10^2$.

It was shown in preliminary experiments that K_e , determined according to equation (4), does not depend on the starting concentrations of the salt and nucleophiles, provided that the starting salt concentration is $< 7.0 \times 10^{-5}\text{M}$ and the concentration of a nucleophile is not $> 1.0\text{M}$. Thus, e.g., for 1,3-dioxolan and $\text{Ph}_3\text{C}^+\text{SbF}_6^-$ we have at -33° : ($[\text{1,3-dioxolan}]$, $[\text{Ph}_3\text{C}^+\text{SbF}_6^-]$ in M, K_e in l mol^{-1}) 2.4×10^{-1} , 1.25×10^{-5} , 1.14; 9.52×10^{-1} , 2.35×10^{-5} , 1.32; 8.34×10^{-1} , 5.75×10^{-5} , 1.08; average $K_e = 1.19 \pm 0.09 \text{ l mol}^{-1}$.

The concentration of triphenylmethyl salt was low enough to shift equilibrium (5) between the ion-pair and



unpaired ions almost completely to the unpaired ions side. According to published measurements^{10,14-16} K_D is ca. 1.4 – $2.5 \times 10^{-4} \text{ mol l}^{-1}$ at 25° in CH_2Cl_2 and virtually independent of the anion structure. Thus, for $K_D =$

⁹ S. Slomkowski, P. Kubisa, and S. Penczek, IUPAC Congress, Helsinki, 1972, paper I-135.

¹⁰ N. Kalfoglou and M. Szwarc, *J. Phys. Chem.*, 1968, **72**, 2233.

¹¹ W. M. Pasika, *Tetrahedron*, 1966, **22**, 557.

¹² A. L. Gatzke and R. Stewart, *Canad. J. Chem.*, 1961, **39**, 1849.

¹³ N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3044.

¹⁴ W. E. Lee and F. E. Treloar, *J. Phys. Chem.*, 1969, **73**, 2458.

¹⁵ F. W. Burns, B. McCarthy, R. M. O'Connor, and D. C. Papper, IUPAC Congress, Helsinki, 1972, paper I-30.

¹⁶ P. Kubisa and S. Penczek, *Makromol. Chem.*, 1971, **144**, 169.

2.5×10^{-4} mol l $^{-1}$ >70% of the triphenylmethyl salt at a concentration of 10^{-4} M will exist as unpaired ions in CH $_2$ Cl $_2$, and at 10^{-5} M this proportion increases to >95%. It can also be assumed that conversion of the carbenium ion into the oxonium derivative, which is larger and has a more dispersed positive charge, should not lower K_D . In our experiments we have used [Ph $_3$ C $^+$ A] $_0$ in the range 1–7 \times 10^{-5} M to ensure a high proportion of unpaired ion so as to neglect the presence of ion-pairs.

Triphenylmethyl cations are known to abstract easily hydride ions from various donors, including acetals and

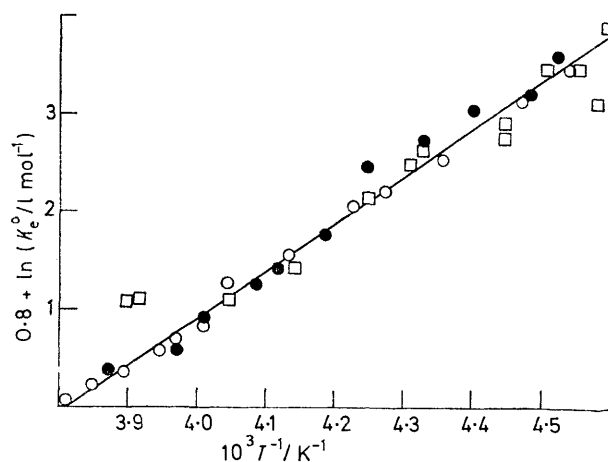


FIGURE 1 Dependence of K_e^0 [equation (1)] on $1/T$ for the equilibrium Ph $_3$ C $^+$ + (EtO) $_2$ CH $_2$ \rightleftharpoons oxonium ion: [Ph $_3$ C $^+$ AsF $_6^-$] $_0$ [(Et $_2$ O) $_2$ CH $_2$] $_0$; ● 2.05×10^{-5} , 6.1×10^{-1} ; ○ 3.16×10^{-5} , 7.21×10^{-1} ; □ 5.46×10^{-5} , 7.8×10^{-1} M

ethers.^{17,18} Therefore equilibrium (1) has been studied at sufficiently low temperatures to suppress the hydride transfer.

Equilibrium constants K_e^0 and thermodynamic parameters * ΔH_e^0 and ΔS_e^0 for equilibrium (1) in CH $_2$ Cl $_2$ at 25 and -73°

Substrate	ΔH_e^0 /kcal mol $^{-1}$	ΔS_e^0 /cal mol $^{-1}$ K $^{-1}$	K_e^0 /l mol $^{-1}$	
			25°	-73°
Water †	-9.3 ± 0.3	-23 ± 1	6.2×10	1.4×10^5
2-Trichloromethyl-1,3-dioxolan	-5.8 ± 0.2	-24 ± 1	8.5×10^{-2}	1.1×10
1,3-Dioxolan	-7.3 ± 0.6	-31 ± 2	3.2×10^{-2}	1.3×10
Dimethoxymethane	-8.3 ± 0.2	-35 ± 1	2.2×10^{-2}	2.2×10
Diethoxymethane	-9.1 ± 0.4	-37 ± 2	3.2×10^{-1}	6.0×10
Dibutyl ether	-9.0 ± 0.2	-31 ± 1	6.7×10^{-1}	1.1×10^3
2-Methyl-1,3-dioxolan	-10.0 ± 0.2	-42 ± 1	1.2×10^{-2}	4.7×10
2-Phenyl-1,3-dioxolan	-10.1 ± 0.6	-35 ± 2	4.6×10^{-1}	2.2×10^3
1,3-Dioxan	-11 ± 1	-44.7 ± 0.6	2.0×10^{-2}	1.8×10^3
1,4-Dioxan	-11.1 ± 0.7	-42 ± 5	4.6×10^{-2}	4.5×10^3
Tetrahydrofuran	-14.0 ± 0.8	-46 ± 3	1.6	1.8×10^5
Diethyl ether	-17	-60	2.3×10^{-1}	2.9×10^5
Tetrahydropyran	-17 ± 1	-60 ± 5	2.3×10^{-1}	1.0×10^6

* Statistical correction applied to K_e^0 by using symmetry numbers. † For comparison, taken from ref. 9.

The equilibrium constants K_e^0 were measured at various temperatures, taking into consideration the symmetry numbers, and the data were used to determine the corresponding enthalpy (ΔH_e^0) and entropy (ΔS_e^0) values. The superscript 0 is used for K_e , ΔH , and ΔS , since for the low concentrations of triphenylmethyl salts equal activity coefficients (γ) for triphenylmethyl and oxonium cations can be assumed. This has been estimated according to the relationship $\ln \gamma = -e^2\chi/2DkT$, where $\chi =$

¹⁷ C. D. Nenitzescu in 'Carbenium Ions,' eds. G. A. Olah and P. von R. Schleyer, Wiley, New York, 1970, vol. II.

$(8\pi ne^2/DkT)^{1/2}$ with n denoting the number of ions per cm 3 .¹⁹ Since the concentrations of the ethers and acetals

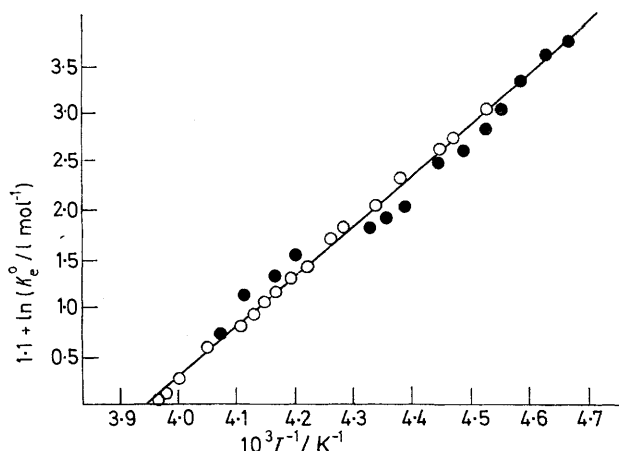


FIGURE 2 Dependence of K_e^0 [equation (1)] on $1/T$ for the equilibrium Ph $_3$ C $^+$ + 2-methyl-1,3-dioxolan \rightleftharpoons oxonium ion measured for triphenylmethyl salts with the anions SbCl $_6^-$ and SbF $_6^-$: ○ [Ph $_3$ C $^+$ SbCl $_6^-$] $_0$ 6.5×10^{-5} , 2-methyl-1,3-dioxolan 4.76×10^{-1} ; ● [Ph $_3$ C $^+$ SbF $_6^-$] $_0$ 7.2×10^{-5} , 2-methyl-1,3-dioxolan 6.76×10^{-1} M

never surpasses 1.0M, γ for these compounds can be taken as close to unity.

Our results confirm the applicability of equation (4) for the analysis of the experimental data. A typical relationship between K_e^0 and $1/T$ for three different starting concentrations of triphenylmethyl salt and dimethoxymethane is shown in Figure 1. Similar results were observed in other systems. The independence of the K_e^0 on the anion structure is shown in Figure 2 for 2-methyl-1,3-dioxolan–triphenylmethyl hexachloroantimonate and

hexafluoroantimonate. Indeed, $\Delta\Delta H_e^0$ and $\Delta\Delta S_e^0$, found by taking the difference between individual functions, calculated by the least-squares method from the data for SbF $_6^-$ and SbCl $_6^-$ are *ca.* 1.0 kcal mol $^{-1}$ and *ca.* 4.5 cal mol $^{-1}$ K $^{-1}$, respectively, while ΔH_e^0 and ΔS_e^0 are (*cf.* Table) 10 kcal mol $^{-1}$ and -42 cal mol $^{-1}$ K $^{-1}$. The standard deviation for both ΔH_e^0 and ΔS_e^0 is *ca.* 10%. The results for the other ethers and acetals are given in the Table.

¹⁸ S. Słomkowski and S. Penczek, *Chem. Comm.*, 1970, 1347.

¹⁹ E. A. Moelwyn-Hughes, 'Physical Chemistry,' Pergamon, London, 1964, p. 896.

DISCUSSION

Data for the equilibria for reactions of linear and cyclic ethers and acetals with triphenylmethyl cation are summarized in the Table. From Figure 2, and from measurements for other nucleophiles not shown on

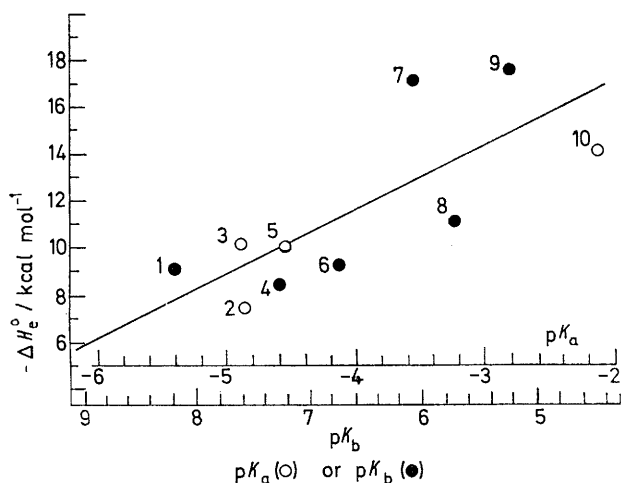


FIGURE 3 Correlation between basicity and enthalpy of equilibrium (ΔH_e°): 1 dibutyl ether; 2 1,3-dioxolan; 3 2-phenyl-1,3-dioxolan; 4 1,2-dimethoxymethane; 5 2-methyl-1,3-dioxolan; 6 1,2-diethoxymethane; 7 diethyl ether; 8 1,4-dioxan; 9 tetrahydropyran; 10 tetrahydrofuran; basicities taken from refs. 20 and 22

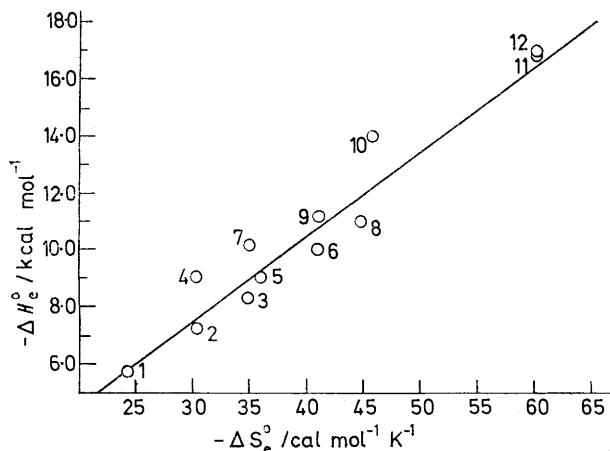


FIGURE 4 Isoequilibrium dependence between ΔH_e° and ΔS_e° (compensation effect) of the reversible reaction $\text{Ph}_3\text{C}^+ + \text{O} \rightleftharpoons \text{Ph}_3\text{C}-\text{O}^+$: 1 2-trichloromethyl-1,3-dioxolan; 2 1,3-dioxolan; 3 dimethoxymethane; 4 dibutyl ether; 5 diethoxymethane; 6 2-methyl-1,3-dioxolan; 7 2-phenyl-1,3-dioxolan; 8 1,3-dioxan; 9 1,4-dioxan; 10 tetrahydrofuran; 11 diethyl ether; 12 tetrahydropyran

the Figures, the equilibrium constants K_e° do not depend on the anion structure. This confirms that these processes involve the unpaired carbenium ion. Thus, this system provides an interesting possibility of quantitative study of the reactivity of the unpaired and paired carbenium ions as well as of the influence of the anion structure on reactivity.

The only previously measured equilibrium constant

²⁰ S. Iwatsuki, N. Tukikawa, M. Okada, and Y. Yamashita, *Kogyo Kagaku Zasshi*, 1964, **67**, 1236.

for the carbenium \rightleftharpoons oxonium ion reaction involved the reaction of triphenylmethyl cation with diethyl ether in acetic anhydride.³ Our value (in CH_2Cl_2 solvent) of K_e° ($2.3 \times 10^{-1} \text{ l mol}^{-1}$) is several times lower than that reported by Smith and Rao ($9.3 \times 10^{-1} \text{ l mol}^{-1}$) for acetic anhydride.² This difference may be due simply to the partial participation of acetic anhydride in oxonium ion formation.

No thermodynamic parameters of the carbenium \rightleftharpoons oxonium ion equilibrium were available before this work. The analysis of our data revealed, as expected, that ΔH_e° is a linear function of the basicity of the corresponding compounds. This correlation is shown in Figure 3 in which the majority of the points are well correlated by a straight line (except, *e.g.* diethyl ether). Thus, ΔH_e° can be expressed in terms of the basicity by the empirical relationships (6a or b).

$$\Delta H_e^\circ = (-2.7pK_a - 22.4) \pm 2.8 \quad (6a)$$

$$\Delta H_e^\circ = (2.4pK_b - 27) \pm 2 \quad (6b)$$

The correlation factor for (6a) and/or for (6b) is quite low ($|\gamma| = 0.7$), but we suppose that both (6a and b) can be used to estimate ΔH_e° . The low accuracy of (6a and b) derives mainly from the uncertainty in the determination of pK_a and pK_b .

Figure 4 shows the isoequilibrium dependence (linear plot of ΔH_e° against ΔS_e°) and indicates that all the nucleophiles react according to the same mechanism. The physical meaning of this dependence and the restrictions involved have recently been comprehensively reviewed.²¹ r Calculated from the data in Figure 4 is 0.97, and, thus, both ΔH_e° and ΔS_e° can, in principle, be estimated from the knowledge of the corresponding pK_a or pK_b values, determined by known methods.²² Although ΔH_e° cannot be determined with sufficiently high accuracy from pK_a or pK_b , much better results are obtained when the actual equilibrium constants K_e° are computed. This is due to the compensation factor.

Since ΔH_e° is a linear function of pK_a (or pK_b) the dependence of the enthalpy of equilibrium on structural and electronic factors can be discussed in the same terms as the similar dependence of the basicity.²² Unfortunately, we cannot at present correlate either ΔH_e° or ΔS_e° directly with the stereoelectric features of the ethers and acetals studied.

Some relationships along these lines can be, however, formulated. Large negative values of the entropies of equilibrium (from -24 for 2-trichloromethyl-1,3-dioxolan to $-60 \text{ cal mol}^{-1} \text{ K}^{-1}$ for tetrahydropyran) are obviously due to the formation of one molecule of the oxonium ion from two participating species. Thus, the number of the translational and rotational degrees of freedom is highly restricted in passing to the oxonium ion.

It could be expected that substitution of the hydrogen atoms by large substituents at the carbon atoms α to

²¹ L. P. Hammett, 'Physical Organic Chemistry,' McGraw-Hill, New York, 1970, ch. 12.

²² E. M. Arnett, *Progr. Phys. Org. Chem.*, 1963, **1**, 1.

the site of reaction, should further lower the entropy of equilibrium, since the formation of the oxonium cation decreases the number of degrees of freedom. This can indeed, be observed when, *e.g.*, 1,3-dioxolan ($\Delta S_e^\circ = -31 \text{ cal mol}^{-1} \text{ K}^{-1}$) is compared with 2-methyl-1,3-dioxolan ($\Delta S_e^\circ = -42 \text{ cal mol}^{-1} \text{ K}^{-1}$) or 2-phenyl-1,3-dioxolan ($\Delta S_e^\circ = -35 \text{ cal mol}^{-1} \text{ K}^{-1}$). Results observed for the much more polar 2-trichloromethyl-1,3-dioxolan ($\Delta S_e^\circ = -24 \text{ cal mol}^{-1} \text{ K}^{-1}$) indicate that the entropy change due to desolvation of the ground state can partially outweigh the influence of the other entropy components. Ritchie²³ has recently stressed the importance of solvent reorganization contributions to free energies of activation.

Apparently, the larger negative entropy change for the six- than for the five-membered rings is due to the greater number of degrees of freedom in the ground state in the cyclic six-membered ethers or acetals than in their five-membered counterparts (tetrahydrofuran *versus* tetrahydropyran and 1,3-dioxolan *versus* 1,3-dioxan). This is obviously due to the presence of individual conformers and the low energy barrier to conformational change.

EXPERIMENTAL

Materials.—Triphenylmethyl salts (AsF_6^- , PF_6^- , SbF_6^-) (Ozark-Mahoning) were purified by several precipitations of the salt from CH_2Cl_2 solution into n-hexane. This was done in vacuum in an apparatus provided with a fitted glass filter and Teflon glass stopcocks (Quickfit) and/or O ring Teflon glass stopcocks (West-Glass). After completely evaporating the solvent on the vacuum line, the

²³ C. D. Ritchie, G. A. Skinner, and V. G. Badding, *J. Amer. Chem. Soc.*, 1967, **89**, 2063.

²⁴ H. Meerwein, E. Battenburg, H. Gold, E. Pfeil, and G. Wilfang, *J. prakt. Chem.*, 1939, **154**, 83.

²⁵ H. Cheradame and P. Sigwalt, *Bull. Soc. chim. France*, 1970, 843.

pure salts were distributed into the thin-walled phials and weighed. Triphenylmethyl hexachloroantimonate was prepared according to ref. 24 and purified as described above. Methylene chloride was rigorously purified essentially as described by Cheradame and Sigwalt,²⁵ and was stored in ampoules over a sodium mirror below 0°. All the ethers and some acetals were commercial samples. Some acetals were synthesized by known procedures.^{26, 27} With the exception of 2-phenyl- and 2-trichloromethyl-1,3-dioxolan, all acetals and ethers were purified by careful fractionation followed by prolonged treatment with CaH_2 on the vacuum line. The purified compounds were stored in vacuum ampoules over liquid Na-K alloy or Na-benzophenone. Purification of 2-phenyl- and 2-trichloromethyl-1,3-dioxolan involved only the CaH_2 treatment.

Instrumentation and Measurement of K_e° .—Equilibrium spectrophotometric measurements were made on a Zeiss double beam apparatus with 1 or 0.1 cm quartz cells placed in a thermostatted metal support or in an optical Dewar flask.

A known amount of a triphenylmethyl salt was mixed with the solvent under vacuum and the concentration of triphenylmethyl cation was measured at room temperature and at -50 to -70° in order to confirm the absence of water (no change of E_{435} after correction for density change). An ether or acetal was then added and equilibrium positions were measured at various temperatures. Temperature was measured with a calibrated thermocouple. Values of K_e° were calculated from the experimental data by equation (4). The stability of solutions and the avoidance of any hydride transfer during the measurements were checked by determining K_e° at the starting temperature when the series of measurements was complete.

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²⁶ P. A. Larent, P. Tarte, and B. Rodriguez, *Bull. Soc. chim. France*, 1959, 945.

²⁷ M. Sulzbacher, E. Bergman, and E. R. Pariser, *J. Amer. Chem. Soc.*, 1948, **70**, 2827.