

$$\log(k_0)_p = a + \delta \log k_0^{\text{res}} = a + (\alpha_{\text{res}} - \beta)_p \delta \log K_p^{\text{res}} \quad (\text{A4})$$

with a being $\log(k_0)_p$ for a reference acid in which the carbanion is stabilized by polar effects only. In a similar way, eq A5 holds for nucleophilic additions.

$$\log(k_0)_N = b + \delta \log k_0^{\text{res}} = b + (\alpha_{\text{res}} - \beta_{\text{nuc}})_N \delta \log K_N^{\text{res}} \quad (\text{A5})$$

Substituting $u(\alpha_{\text{res}} - \beta)_p$ for $(\alpha_{\text{res}} - \beta_{\text{nuc}})_N$ (eq A2) and $v(\delta \log$

K_p^{res}) for $\delta \log K_N^{\text{res}}$ in eq A5 yields

$$\log(k_0)_N = b + uv(\alpha_{\text{res}} - \beta)_p \delta \log K_p^{\text{res}} \quad (\text{A6})$$

From eq A4 we obtain

$$(\alpha_{\text{res}} - \beta)_p \delta \log K_p^{\text{res}} = \log(k_0)_p - a \quad (\text{A7})$$

Combining eqs A6 and A7 leads to

$$\log(k_0)_N = c + uv \log(k_0)_p \quad (\text{A8})$$

which is equivalent to eq A1 with slope = uv and $c = b - auv$.

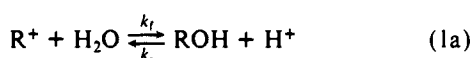
Kinetic Method for the Measurement of the pK_R Value of the Triphenylmethyl Cation in the Aqueous Standard State

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Abstract: A kinetic method is presented for the measurement directly in the aqueous standard state of the equilibrium constant K_R for the reaction $\text{Ph}_3\text{C}^+ + \text{H}_2\text{O} = \text{Ph}_3\text{COH} + \text{H}^+$. The basis of the procedure is direct measurement of the rate constant k_f for the reaction proceeding in the forward direction with the technique of laser flash photolysis. The rate constant k_r for the reverse reaction is measured by following oxygen exchange in a labeled alcohol in a weakly acidic (0.005 M HCl) solution. At 25 °C in water, $k_f = (1.68 \pm 0.06) \times 10^5 \text{ s}^{-1}$, $k_r = (5.79 \pm 0.29) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$, and the value for pK_R calculated from their ratio is -6.46 ± 0.03 . The value for k_r is based on a slight extrapolation from 5% acetonitrile in water. The value for k_f is measured in water. This directly measured value for pK_R provides a test of the validity of the acidity function and excess acidity methods commonly employed to determine pK values for weak bases where the equilibrium with the conjugate acid form can only be studied in strong acids. Values of pK_R previously reported for Ph_3C^+ based upon these approaches vary from -5.85 to -6.89 , although the range is smaller, -6.44 to -6.89 , if data obtained in concentrated HCl are omitted. The conclusion is that these methods *do* lead to pK_R values in reasonable agreement with the directly measured number.

The measurement of the equilibrium constant pK_R for a carbenium ion-carbinol equilibrium (eqs 1a,b) can be carried out in a straightforward manner when the value lies within the range of about 2–12. In such a case, R^+ and ROH coexist at equi-



$$K_R = \frac{[\text{ROH}][\text{H}^+]}{[\text{R}^+]} = \frac{k_f}{k_r} \quad (\text{1b})$$

librium in significant amounts in some aqueous solution that is ideal or close to ideal. Thus, when their concentrations (or ratio of concentrations) are measured, the equilibrium constant can be calculated from eq 1b with use of the known $[\text{H}^+]$ concentration. This situation is found with highly stabilized carbenium ions,² such as tropylium ions and triarylmethyl cations bearing at least one *p*-dimethylamino substituent. However, for less stable carbenium ions, nondilute acids are required in order to obtain solutions with significant amounts of cation present, for example, $>45\%$ H_2SO_4 in the case of the parent triphenylmethyl cation.³ In such solutions, concentrations cannot be equated to activities,⁴ and some form of extrapolation is needed to obtain the thermodynamic pK_R value in the aqueous standard state. The same problem arises

in the measurement of pK_a values of the conjugate acids of weak bases which protonate only in concentrated acids. These pK_a and pK_R values have considerable importance in the understanding of quantitative structure-activity relationships as well as in the analysis of the mechanisms of reactions that occur in nondilute acids. In consequence, there has been an extensive effort to develop methods for their determination. This has generally involved the establishment of acidity scales that incorporate the necessary activity coefficients and activities in such a way that pK values can be calculated from knowledge of the measured ionization ratios $[\text{R}^+]:[\text{ROH}]$ or $[\text{BH}^+]:[\text{B}]$. A number of approaches have been suggested, with two now the most widely used, the Hammett acidity function method and the excess acidity method. These procedures, particularly those involving acidity functions, have been reviewed on a number of occasions.⁵ The details will not be discussed here; the acidity scales are usually based on some assumption of equivalency or proportionality of a ratio of activity coefficients and activities. In general, the acidity function and excess acidity methods give pK values that are in reasonable agreement, although differences are occasionally large for systems that require study in very concentrated acids. The acidity function method has been criticized because, even for structurally related systems, there is frequently not the exact parallelism of \log (ionization ratios) required by the basic postulate.⁶ It has also been pointed out that the various acidity function scales do not

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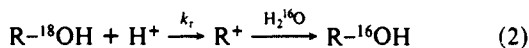
Table I. Values of k_f , k_r , and $\log(k_f/k_r)$ at 25.0 °C in Acetonitrile–Water Solutions for Triphenylcarbenium–Triphenylcarbinol Equilibration

% acetonitrile ^a	k_f , ^b M ⁻¹ s ⁻¹	k_r , s ⁻¹	$\log K_C = \log(k_f/k_r)$
0	$(5.79 \pm 0.29) \times 10^{-2c}$	$(1.68 \pm 0.06) \times 10^{5d}$	6.46 ± 0.03
5	$(4.20 \pm 0.14) \times 10^{-2}$	$(1.78 \pm 0.07) \times 10^{5d}$	6.62 ± 0.03
10	$(3.03 \pm 0.12) \times 10^{-2}$	$(1.82 \pm 0.06) \times 10^{5d}$	6.78 ± 0.02
15	$(2.10 \pm 0.10) \times 10^{-2}$	$(1.89 \pm 0.05) \times 10^{5d}$	6.95 ± 0.02
20	$(1.36 \pm 0.05) \times 10^{-2}$	$(1.94 \pm 0.06) \times 10^{5d}$	7.14 ± 0.02
20		$(1.89 \pm 0.04) \times 10^{5e}$	
30	$(7.72 \pm 0.23) \times 10^{-3}$	$(1.90 \pm 0.03) \times 10^{5e}$	7.39 ± 0.02
40	$(3.93 \pm 0.05) \times 10^{-3}$	$(1.98 \pm 0.02) \times 10^{5e}$	7.70 ± 0.01
50	$(2.70 \pm 0.08) \times 10^{-3}$	$(2.06 \pm 0.03) \times 10^{5e}$	7.89 ± 0.02
50	$(2.62 \pm 0.06) \times 10^{-3f}$		
50	$(2.65 \pm 0.09) \times 10^{-3g}$		
60	$(2.28 \pm 0.04) \times 10^{-3}$	$(2.07 \pm 0.03) \times 10^{5e}$	7.95 ± 0.01
70	$(2.27 \pm 0.03) \times 10^{-3}$	$(2.06 \pm 0.03) \times 10^{5e}$	7.96 ± 0.01
80	$(2.60 \pm 0.03) \times 10^{-3}$	$(1.91 \pm 0.03) \times 10^{5e}$	7.87 ± 0.01
90	$(5.50 \pm 0.09) \times 10^{-3}$	$(1.40 \pm 0.03) \times 10^{5e}$	7.41 ± 0.01

^a Volume percent. ^b $k(\text{Ex})/[\text{H}^+]$ for experiments in 0.005 M HCl, unless otherwise noted. ^c Obtained by extrapolation, see text. ^d Triphenylacetate as precursor. ^e Triphenylmethyl *p*-cyanophenyl ether as precursor. ^f 0.01 M HCl. ^g 0.015 M HCl.

merge smoothly into the pH scale, as they should.⁷ On the other hand, an analysis of the relationships of pK values with various physicochemical parameters has suggested that in certain cases the acidity function method provides values that are more internally consistent.⁶

In this paper, a kinetic method is described for the measurement of pK_R values directly in the aqueous standard state. This equilibrium constant is a ratio of rate constants for the reactions in the forward and reverse directions, with k_f defined in units of s⁻¹ and k_r in units of M⁻¹ s⁻¹ (eq 1). For an unstable cation such as triphenylmethyl, solutions in the pH range contain immeasurably small concentrations of the cation under equilibrium conditions. The kinetic approach is made possible by the generation of nonequilibrium amounts of cation with the technique of laser flash photolysis. With this method, carbenium ions can be generated in aqueous solutions and rate constants for their reaction with solvent directly measured.⁸ This rate constant is k_f of eq 1. The other rate constant k_r can be obtained from a kinetic study of oxygen exchange in dilute acid.



As will be argued, this exchange proceeds by rate-limiting H⁺-catalyzed conversion of the alcohol to the carbenium ion, with a second-order rate constant that is equal to k_r .

This paper describes the application of the kinetic method to the measurement of the pK_R value of the triphenylmethyl cation. There have been several previous determinations with use of the acidity function and excess acidity methods (see later text). The result of this study provides a test of the validity of these procedures. It can be noted that the carbenium ion–carbinol system is ideally suited to a kinetic approach for the measurement of pK. The reaction in the thermodynamically favored direction, cation to alcohol, is for many R⁺ “slow”, that is, not diffusion-controlled. Rate constants for many triarylmethyl and diarylmethyl cations are in the time regime accessible with nanosecond laser flash photolysis equipment.^{8d} Moreover, oxygen exchange in the alcohol is a convenient way to measure k_r . For proton transfers involving weak oxygen and nitrogen bases, on the other hand, the deprotonation reaction is diffusion-limited,⁹ and for most systems there is no method for measuring the rate constant for protonation.¹⁰

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Table II. Activation Parameters^a for the Decay of the Triphenylmethyl Cation in Acetonitrile–Water Mixtures

% acetonitrile ^b	ΔS^\ddagger , J mol ⁻¹ K ⁻¹	ΔH^\ddagger , kJ mol ⁻¹
0 ^c	-83 ± 3	18.5 ± 1.0
30	-70 ± 4	21.8 ± 1.2
50	-60 ± 3	24.6 ± 1.0
70	-64 ± 5	23.4 ± 1.4
90	-87 ± 4	16.8 ± 1.2

^a Rate constants measured at five to seven temperatures in the range 0–70 °C. ^b Percent by volume. ^c Cation produced by photolysis of triphenylacetic acid (0.15 mM) in the presence of potassium peroxydisulfate (25 mM) at pH 8. In the presence of peroxydisulfate, the photochemical yield of the triphenylmethyl cation is significantly increased (Steenken, S. Unpublished material).

Equilibrium constants for systems involving a reactive intermediate have been previously obtained in two important cases: the formation of tetrahedral intermediates from ester precursors¹¹ and keto–enol tautomerization.¹² In each system, the procedure relied upon being able to generate the thermodynamically unstable intermediate in nonequilibrium amounts, such that its rate constant for conversion to the more stable form could be directly measured.

Results

Rate Constants for Hydration of Cation. The methods for directly studying the decay of triphenylmethyl cation in aqueous solutions have been previously described.^{8a,d,f} For solutions that contained greater than 20% acetonitrile, triphenylmethyl *p*-cyanophenyl ether was employed as the precursor. This compound undergoes an efficient heterolysis upon excitation, generating the cation and the *p*-cyanophenolate anion.^{8a,d} In more aqueous solutions, this ether is not sufficiently soluble and the precursor employed was the triphenylacetate anion. This compound generates the triphenylmethyl cation at high laser intensities in a sequence of reactions involving the sequential absorption of three photons during the laser pulse.^{8f} The cation-generating step is the photoionization of the triphenylmethyl radical.

A requirement for the calculation of the desired equilibrium constant is that the rate constant measured in the flash photolysis

(10) (a) Attempts have been made to estimate pK_a values for the conjugate acids of nitrogen bases, R₂NH, by coupling rate constants for N–H exchange with a value for the deprotonation rate constant characteristic of a diffusion-controlled reaction.^{10b–e} In addition to uncertainty in the latter number, it has been suggested that in some cases the exchange rate constant is not equal to the rate constant for protonation, since the protons in R₂NHH⁺ may not achieve conformational equilibrium.^{10d–h} (b) Fersht, A. R. *J. Am. Chem. Soc.* **1971**, *93*, 3504. (c) Martin, R. B. *J. Chem. Soc., Chem. Commun.* **1972**, 793. (d) Martin, R. B.; Hutton, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 4752. (e) Kresge, A. J.; Capen, G. L. *Ibid.* **1975**, *97*, 1795. (f) Perrin, C. L. *Ibid.* **1974**, *96*, 5628, 5631. (g) Perrin, C. L.; Johnston, E. R. *Ibid.* **1979**, *101*, 4753. (h) McClelland, R. A.; Reynolds, W. F. *Can. J. Chem.* **1979**, *57*, 2896.

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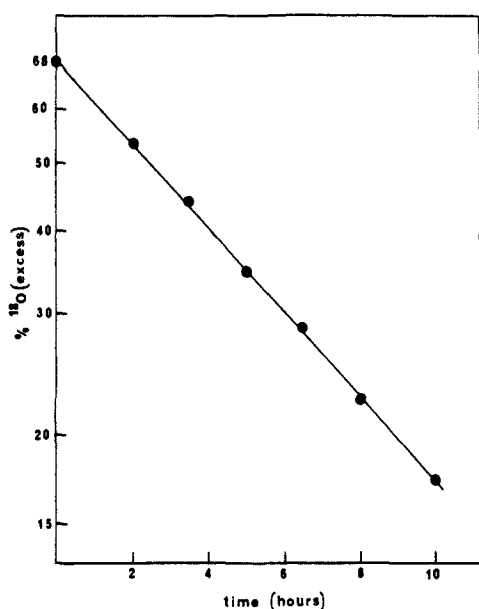


Figure 1. Percent excess ^{18}O as a function of time for triphenylmethanol in 30% by volume acetonitrile containing 0.005 M HCl at 25 °C. Note that y axis is plotted in logarithmic form.

experiments refers to the reaction of ground-state cation with the solvent. Arguments have been presented that this is the case.^{8c} In the present instance, there is good evidence in the excellent match of the transient spectrum with that obtained for solutions of the triphenylmethyl cation in concentrated sulfuric acid solutions.^{8a,d} In addition, there is excellent agreement of the rate constants obtained with the two precursors (see the entries in 20% acetonitrile in Table I), in spite of the very different photochemistry involved in generating the cation.

The rate constants are presented in Table I under the heading k_f . These numbers have been measured in a thermostated cell at 25 ± 0.1 °C and are, thus, slightly larger than those previously reported^{8a,d,f} at 20 ± 1 °C. The error reported in Table I is the standard deviation obtained over four to six kinetic runs. The trend in k_f , a small increase from 0% to ~70% acetonitrile followed by a decrease, has been noted before and seems to be commonly observed for cations in this solvent mixture.^{8d,e} Activation parameters in selected solvent mixtures are given in Table II. The reaction is characterized by a large negative entropy of activation. This is similar to values that have been observed on reaction of water with di- and trialkoxy carbocations and can be explained in terms of solvent immobilization by the H^+ being produced in the reaction.^{8h,j} There is little change in the activation parameters with changing solvent, except in the acetonitrile-rich solutions.

Triphenylmethanol Oxygen Exchange. These experiments were carried out with ^{18}O -labeled triphenylmethanol prepared by hydrolyzing triphenylmethyl chloride with [^{18}O]water. Small quantities of the labeled alcohol were dissolved in 0.5–5-L volumes of aqueous acetonitrile solutions containing hydrochloric acid. At appropriate times, the alcohol was isolated and subjected to mass spectral analysis, with the ratio of parent ions at m/z 262 and m/z 260 being the quantity measured. The excess percent ^{18}O was calculated with the formula¹³

$$\% \text{ excess } ^{18}\text{O} = 99.8 \left(\frac{R - R_0}{1.002 + R - R_0} \right) \quad (3)$$

where R and R_0 are, respectively, the 262:260 ratios obtained with the sample in question and with unlabeled triphenylmethanol. This calculation corrects for the presence of other isotopes of carbon and hydrogen and also accounts for the 0.2% ^{18}O that is naturally occurring. First-order rate constants $k(\text{Ex})$ were calculated as

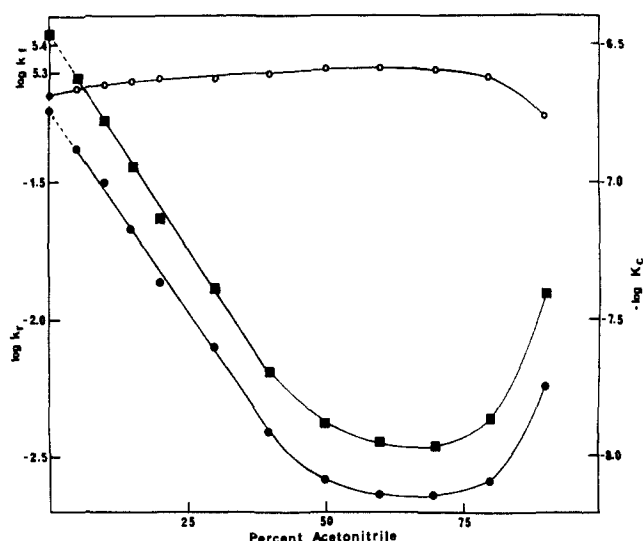


Figure 2. Dependencies of $\log k_f$, $\log k_r$, and $-\log K_C$ on acetonitrile content.

slopes of plots of $\ln(\% \text{ excess } ^{18}\text{O})$ versus time. A representative kinetic run is shown in Figure 1. The labeled alcohol contained initially 68% ^{18}O , and the exchange was in general followed for 2–3 half-lives. The kinetic plots were excellently linear.

The numbers calculated in these kinetic runs were pseudo-first-order rate constants, since the exchange should be dependent on H^+ concentration. This point was investigated in 50% acetonitrile where experiments were carried out in 0.005, 0.01, and 0.015 M HCl. The values of $k(\text{Ex})$ were 1.35×10^{-5} , 2.62×10^{-5} and $3.98 \times 10^{-5} \text{ s}^{-1}$, respectively, showing excellent proportionality in $[\text{H}^+]$. In all other solvents, rate constants were obtained only in 0.005 M HCl and the second-order rate constants calculated by dividing by the acid concentration. Values from 5% acetonitrile to 90% acetonitrile are listed under the heading k_f in Table I. The errors given with each are the deviations in the slopes of the kinetic plots.

Unfortunately, triphenylmethanol proved not to be sufficiently soluble in the crucial solvent, 100% water, for exchange experiments to be carried out. The value for k_f listed in Table I for water is, therefore, based on extrapolation. A plot of $\log k_f$ versus percent acetonitrile is linear from 5% to 40% (Figure 2), and the assumption was made that this relationship extends to pure water. The error given for k_f in water is the standard deviation of the intercept of this linear regression line.

An important question is whether the second-order rate constant for H^+ -catalyzed exchange is the same as k_r , the rate constant for formation of the triphenylmethyl cation from the alcohol. Bunton has good evidence with (*p*-methoxyphenyl)phenylmethanol for a free carbenium ion intermediate in that oxygen exchange in aqueous acetonitrile containing greater than 5% water is accompanied by 100% racemization of optically active starting material.¹⁴ Triphenylmethanol is more sterically congested than this alcohol and, judging from a comparison of pK_R values,^{8d} more readily forms the carbenium ion. Thus, it seems very likely that its oxygen exchange must also involve a free carbenium ion. Certainly the flash photolysis experiments demonstrate that both the triphenylmethyl cation and the (*p*-methoxyphenyl)phenylmethyl cation^{8b,d} are sufficiently long-lived in aqueous solutions to exist as free ions. A second concern is whether the cation, once formed, reacts with solvent water or with a water molecule containing its original oxygen. The experiments were carried out with solvent in vast excess over alcohol, so that the former must be the case. In other words, the rate-limiting step in the exchange must be the formation of the cation from the alcohol. Finally, it should be noted that the k_f values refer to loss of ^{18}OH from the alcohol. Since the equilibrium constants are intended to represent normal

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Table III. Values of pK_R at 25 °C for the Triphenylmethyl Cation Obtained by Acidity Function, Excess Acidity, and Kinetic Methods

pK _R	acid ^a	method
-6.63	H ₂ SO ₄	acidity function ^b
-6.44	H ₂ SO ₄	acidity function ^c
-6.12	HCl	acidity function ^d
-6.89	HClO ₄	acidity function ^e
-6.60	HNO ₃	acidity function ^e
-6.47	H ₂ SO ₄	excess acidity ^f
-5.85	HCl	excess acidity ^g
-6.46		kinetic method

^a Aqueous acid in which ionization ratios were measured. ^b Reference 3. ^c Arnett, E. M.; Buschick, R. D. *J. Am. Chem. Soc.* **1964**, *86*, 1564. ^d Arnett, E. M.; Mach, G. W. *Ibid.* **1986**, *88*, 1177. ^e Deno, N. C.; Berkheimer, H. E.; Evans, W. L.; Peterson, H. J. *Ibid.* **1959**, *81*, 2344. ^f Cox, R. A.; Yates, K. *Can. J. Chem.* **1984**, *62*, 2155. ^g Cox, R. A.; Yates, K. *Can. J. Chem.* **1981**, *59*, 2166.

isotopic distribution, a small correction for the primary ¹⁸O:¹⁶O kinetic isotope effect may be necessary. However, this isotope effect is very small and probably not outside the experimental error in the measurement of the exchange rate constant.

Discussion

Values of k_f/k_r are given in logarithmic form in Table I. This ratio is the concentration equilibrium constant, $K_C = [\text{ROH}][\text{H}^+]/[\text{R}^+]$, for the particular combination of acetonitrile:water. A plot of the dependency of $\log K_C$ on acetonitrile content is shown in Figure 2. Because of the relative insensitivity of k_f to the solvent variation, most of the change that occurs in K_C can be traced to changes in k_r . As illustrated in Figure 2, the curves for $-\log k_c$ and $\log k_r$ parallel one another quite closely.

The variation of K_C with solvent composition is given by

$$K_C = \left(\frac{f_{\text{R}^+} a_w}{f_{\text{H}^+} f_{\text{ROH}}} \right) K_R \quad (4)$$

where the terms in f represent medium effect activity coefficients,⁴ a_w is the activity of water, and K_R is the thermodynamic equilibrium constant with water as the standard state. The quantities f and a_w are defined in such a way that their values are unity in water. In qualitative terms, a_w decreases with increasing acetonitrile content,¹⁵ and $f_{\text{R}^+}/f_{\text{H}^+}$ should also decrease. The latter can be predicted since the hydronium ion is strongly solvated by water molecules, so that the removal of water should result in its activity coefficient increasing relative to that of the more poorly solvated Ph₃C⁺.⁴ Each of the above effects acts in such a way to decrease K_C as acetonitrile is added to water. The value, however, increases, at least from 0% to 60% acetonitrile. This must mean, therefore, that the dominant factor in determining the behavior is the activity coefficient of the alcohol. This decreases on adding acetonitrile, since the hydrophobic alcohol is very poorly solvated by water molecules. The effect would appear to be quite large, as judged by the qualitative examinations of the solubilities of triphenylmethanol that accompanied the exchange experiments. In other words, as acetonitrile is added to water, the equilibrium of eq 1 shifts to the right-hand side for the simple reason that triphenylmethanol is better solvated.

Table III summarizes pK_R values previously reported for the triphenylmethyl cation with the acidity function and excess acidity methods. There is reasonable agreement between the two methods, although the values do depend somewhat on the mineral acid in which measurements were made. The values vary from -5.85 to -6.89, although the range is smaller, -6.44 to -6.89, if the two numbers obtained from HCl are omitted. The value for pK_R measured kinetically in this work is -6.46 ± 0.03. This represents the first example where a pK value has been obtained directly in the standard state for a (pseudo)acid as strong as the triphenylmethyl cation, so that the acidity function and excess acidity procedures can be subjected to experimental verification. The conclusion is that with this system, at least, these extrapolations do lead to pK values that are close to the directly measured one. The assumptions inherent in these procedures have been questioned in the past.^{16,17} There has in particular been the suggestion that, in addition to random experimental error, the pK values obtained from any acidity function type analysis are the true pK plus an indeterminate constant.¹⁷ The presence of such constants may account for the dependency of pK_R on mineral acid. However, it is clear that for data obtained in H₂SO₄, the acid most commonly employed in studying weakly basic systems, that the value of the constant must be close to zero for the triphenylmethyl cation. This acid provides pK_R values with use of both the acidity function and excess acidity methods that are within experimental error the same as the directly measured one.

Experimental Section

Triphenylmethyl *p*-cyanophenyl ether was from a previous study.^{8a} Triphenylmethanol-¹⁸O was prepared by adding triphenylmethyl chloride (4 mmol) to a solution of 80% [¹⁸O]water (6 mmol) and pyridine (4.5 mmol) in 5 mL of acetonitrile. The latter was cooled in an ice bath during the addition, and the mixture was then allowed to stand at room temperature for 2 h. Acetonitrile was removed with a rotary evaporator, water was added, and the product was obtained by filtration with washings of ice-cooled water. There was a quantitative recovery of triphenylmethanol analyzed as having 68.2% ¹⁸O. The difference from the percentage originally present in the labeled water was likely due to traces of normal water in the acetonitrile solvent.

Laser flash photolysis studies were carried out as previously described.^{8a,d} Solutions were slowly flowed through a thermostated UV cuvette with a temperature sensor shortly after the sampling portion.

Oxygen-exchange experiments were carried out by dissolving 20–100 mg of triphenylmethanol-¹⁸O in 50 mL of acetonitrile. After being thermostated at 25.0 °C, this solution was added all at once to 0.5–5.0 L of an aqueous acetonitrile solution containing HCl that had also been thermostated at 25.0 °C. The resulting solution was allowed to remain in the thermostating bath. The larger volumes were required for the water-rich solutions in order to dissolve the triphenylmethanol. At appropriate times one-tenth of the volume was removed, 1 g of sodium carbonate added, and the solvent evaporated, initially with a rotary evaporator and to dryness with a freeze dryer. The triphenylmethanol was separated from the sodium carbonate remaining by dissolving in 1–2 mL of ether, followed by filtration and removal of the ether. The alcohol was analyzed with a VG70-250S mass spectrometer.

Acknowledgment. R.A.M. thanks the Petroleum Research Fund, administered by the American Chemical Society, and the Natural Sciences and Engineering Research Council of Canada for support.

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