Communications to the Editor

Protonation of Phthalic Acid: an Unusual Acylium-Carboxonium Rearrangement

Sir:

Protonations of carbonyl compounds have been extensively studied by Olah.[1,2] Many protonated acids and acyl halides cleave to acylium ions upon temperature elevation.[2,3] Cyclic and linear aliphatic acid anhydrides cleave asymmetrically upon protonation to the corresponding acylium ion and protonated carboxyl function.[2] However, aromatic acid anhydrides were reported to undergo only diprotonation, without cleavage,[4] and no satisfactory explanation was given to this anomaly. We report the protonation of benzene dicarboxylic acids and their cleavage in magic acid-SO_2 to the corresponding acylium ions. We submit that diprotonated phthalic acid (**1c**) cleaves to a stable species **2c** (or **2c′**) in which, unlike **2a** and **2b**, an overall degenerate tautomeric shift occurs. In this process a molecule of water, formally, oscillates between two adjacent sites.

Terephthalic and isophthalic acids form in magic acid-SO_2 at −30 °C the corresponding doubly protonated species, viz., **1a** and **1b**, respectively (Table I). Heating of **1a** and **1b** to +30 °C for several minutes revealed additional sets of bands in the ^{1}H NMR spectra (Table I), which are assigned to **2a** and **2b**, i.e., benzene rings bearing an acylium ion and a protonated carboxyl group. The ratios **1a**:**2a** and **1b**:**2b** are approximately 3:2.[6] When phthalic acid was transformed to the doubly protonated species **1c** (Table I), the OH^+ band was observed only below −50 °C and even then it was relatively broad. The exceptional behavior of the ortho substituted diprotonated species **2c** is analogous to the behavior of protonated dimethyl phthalate.[7] It has already been pointed out that the two carbonyls are close together with both protons mutually bonded. Heating **1c** for a few minutes produced a new set of bands at −30 °C (Table I). Contrary to **1a** and **1b**, the bands of **1c**, have completely disappeared. No OH^+ absorption was observed even at −100 °C. The symmetry of this spectrum (AA′BB′ pattern) can be rationalized prima facie either by the formation of a diprotonated anhydride, viz., **3** or a diacylium ion. The same ^{1}H NMR spectrum is obtained when phthalic anhydride

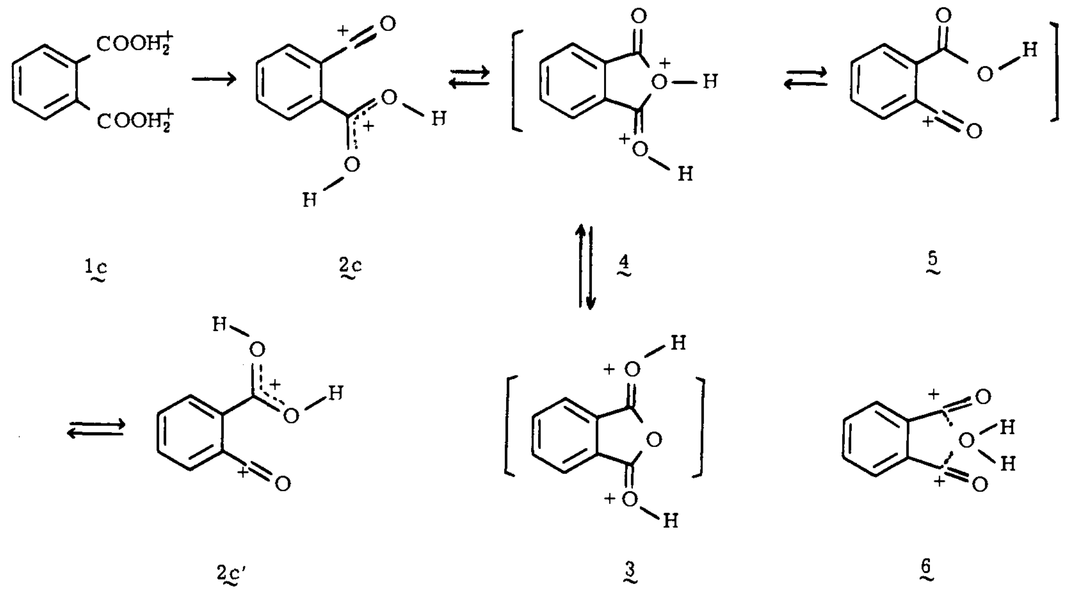

Table I. Proton and Carbon Chemical Shifts of Protonated Benzenedicarboxylic Acids and Acylium Ions[a]

	Diprotonated acid (**1**)		Acylium ion (**2**)	
Acid	^{1}H NMR[b,d]	^{13}C NMR[c,d,f]	^{1}H NMR[b,e]	^{13}C NMR[c,e,f]
(a) Terephthalic acid	8.68 (s, 4 H, arom) 12.77 (s, 4 H, OH^+)	127.9 (1), 131.5 (2), 179.4 (carbonyl)	8.91, 9.17 (AA′BB′, 4 H, arom), 13.38 (s, 2 H, OH^+)	99.4 (1), 146.3 (2), 133.9 (3), 140.8 (4), 147.2 (carbonyl), 178.1 (carbonyl)
(b) Isophthalic acid	8.36, 9.00 (A_2B, 3 H), 9.30 (s, 1 H), 12.54 (s, 4 H, OH^+)	121.0 (1), 134.9 (2), 140.9 (4), 130.9 (5), 178.0 (carbonyl)	8.57, 9.42 (A_2B, 3 H, arom), 9.74 (s, 1 H) 13.84 (s, 2 H, OH^+)	92.8 (1), 148.2 (2), 123.7 (3), 143.4 (4), 133.2 (5), 147.4 (6), 176.0 (carbonyl), 158.5 (carbonyl)
(c) Phthalic acid	8.48 (s, 4 H, arom), 13.34 (s, 4 H, OH^+)[g]	120.7 (1), 133.6 (3), 138.0 (4), 181.0 (carbonyl)	8.82 (m, 2 H, arom), 9.20 (m, 2 H, arom)	118.6 (1), 134.5 (3), 140.7 (5), 164.7 (carbonyl)

[a] 0.1 M solution in a 1:1 v/v SO_2:magic acid in sealed NMR tubes. [b] At 100 MHz, Varian HA 100D spectrometer, in ppm relative to hexamethylsiloxane. [c] At 20 MHz, Varian CFT-20, in ppm relative to tetramethylsilane; acetone-d_6 in a capillary served for locking, carbonyl absorption at 204.3 ppm relative to Me_4Si was used for calibration. [d] At −30 °C. [e] Sample heated for several minutes to +30 °C, spectrum was run at −30 °C. [f] Numbers in parentheses refer to the corresponding carbon atom. [g] Below −50 °C.

reacts at −70 °C with magic acid-SO_2. Formation of a diacylium ion is ruled out since no appropriate increase of the water band was observed.[8] The aromatic protons of **2c** show a significant downfield shift compared with **1c** (Table I) and with diprotonated phthalimid; this may also rule out the formation of diprotonated phthalic anhydride **3**.[9]

An insight into system **2c**, is obtained from its ^{13}C NMR spectrum (Table I). The chemical shifts of the carbonyl carbons of **2c** show an intermediary value of the two carbonyl carbons of **2a** (δ ($COOH_2^+$) 178.1 ppm, δ(CO^+) 147.2 ppm, δ average 162.6 ppm, δ observed 164.7 ppm) (Table I). The ipso carbon atoms of **2c** appear at 118.6 ppm, the ipso carbon atoms of **2a** appear at 99.4 and 140.8 ppm, average 120.1 ppm (Table I). These data together with the disappearance of the OH^+ band and the downfield shift of the aromatic protons of **2c** are in agreement with the following conclusion: A fast migration (in the NMR scale) of a molecule of water occurs between the two adjacent carbonyls of **2c**. This fast rearrangement occurs either in the following process: **2c** $\rightleftharpoons$ **4** $\rightleftharpoons$ **5** $\rightleftharpoons$ **2c′**, a degenerate process, or by the formation of a single species, e.g., **6**. It seems that **6** need not show an averaging of the chemical shifts, of the ipso and the carbonyl carbon atoms and therefore the acylium–carboxonium rearrangement **2c** $\rightleftharpoons$ **2c′** is preferred.

References and Notes

(1) G. A. Olah and A. M. White, *Chem. Rev.*, **70,** 561 (1970), and references cited therein.

(2) G. A. Olah, J. M. Denis, and P. Westerman, *J. Org. Chem.,* **39,** 1206 (1974); J. W. Larsen and P. A. Bouis, *ibid.*, **38**, 1415 (1973); D. A. Tomalia, *ibid.*, **34**, 2583 (1969); J. O. Knobloch and F. Ramirez, *ibid.*, **40**, 1101 (1975).

(3) J. W. Larsen and P. A. Bouis, *J. Am. Chem. Soc.*, **97**, 4418 (1975); G. A. Olah and M. White, *ibid.*, **89**, 7072 (1967); G. A. Olah and P. W. Westerman, *ibid.*, **95**, 3706 (1973).

(4) G. A. Olah, Y. K. Mo, and J. L. Grant, *J. Org. Chem.*, **38**, 3207 (1973).

(5) N. C. Deno, C. V. Pittman, and M. J. Wisotsky, *J. Am. Chem. Soc.*, **86,** 4370 (1964).

(6) Heating the samples up to +70 °C, or prolonged heating at +30 °C, did not change these ratios in the spectrum recorded at −30 °C (Table I). It seems that an equilibrium process, viz., 1a $\rightleftharpoons$ **2**a + H_2O and 1**b** $\rightleftharpoons$ **2b** + H_2O is involved. In neat magic acid the ratios of 1a:**2**a and **1b**:**2b** are 2:3, respectively.

(7) D. Bruck and M. Rabinovitz, *J. Am. Chem. Soc.*, 9**8**, 1599 (1976).

(8) Quenching experiments with methanol never gave any dimethyl phthalate; however, monomethyl phthalate is the main quenching product. A similar observation has also been made in the study of protonation of anhydrides.[2]

(9) Protonation of phthalimid which is isoelectronic to phthalic anhydride shows a similar chemical shift of the aromatic protons to **1c** and not to **2c.** Cf. G. A. Olah et al., *J. Am. Chem. Soc.,* **90**, 6464 (1968).

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Vestiges of the "Inverted Region" for Highly Exergonic Electron-Transfer Reactions

Sir:

The Marcus theory for outer-sphere electron-transfer reactions predicts that a plot of log k_{12} (k_{12}, the rate constant for the electron-transfer reaction) vs. $\Delta G°_{12}$ (the free energy change for the electron-transfer reaction) for constant reorganization energy should be parabolic. One remarkable feature of the theory is the so-called "inverted" region; when $-\Delta G°_{12} > 2(\Delta G^*_{11} + \Delta G^*_{22})$ where $(\Delta G^*_{11} + \Delta G^*_{22})/2$ is the intrinsic electron-transfer barrier, the reaction rate constant should *decrease* as the free energy change becomes more favorable. When k_{12} is calculated from eq 1[1]

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \tag{1a}$$

$$\log f_{12} = \frac{(\log K_{12})^2}{4 \log \left(\dfrac{k_{11}k_{22}}{Z^2}\right)} \tag{1b}$$

(where k_{11} and k_{22} are the self-exchange rates for the oxidizing and reducing couples, respectivel, K_{12} is the equilibrium constant for the cross-reaction, and Z is a collision number usually taken as 10^{11} M^{-1} s^{-1}), the point of crossover into the inverted region may be expressed as (eq 1c).

$$\log K_{12} = 2 \log (Z^2/k_{11}k_{22}) \tag{1c}$$

It is apparent from condition 1c that crossover into the inverted region is favored when *both* K_{12} and $k_{11}k_{22}$ are large. Few opportunities for systematic exploration of the inverted region arise when both reactants are in their ground electronic states since K_{12} is not sufficiently large. On the other hand, excited state systems with small reorganization energies provide excellent probes of this region. Rehm and Weller sought evidence for inverted behavior in the electron-transfer quenching of hydrocarbon fluorescence. The quenching rate constants were, however, found to lie at the diffusion-controlled limit from $\Delta G°_{12} = -10$ to -62 kcal mol^{-1} even though onset of the inverted region is expected at $\Delta G°_{12} \sim -15$ kcal mol^{-1}.[2] In the present study we have used inorganic oxidants with small reorganization energies to quench the luminescence of polypyridineruthenium(II) complexes. For this series with $k_{11}k_{22} \sim 10^{16}$ M^{-2} s^{-2} ($\Delta G^*_{11} + \Delta G^*_{22} \sim 8$ kcal mol^{-1}) and $-\Delta G°_{12} = 10$ to 46 kcal mol^{-1} (inversion predicted at $-\Delta G°_{12} > 16$ kcal mol^{-1}), we do find evidence for diminished rate constants in the inverted region.

We have studied the quenching of the luminescence of the charge-transfer excited states of two polypyridineruthenium(II) complexes RuL_3^{2+} (L = 2,2′-bipyridine or 4,4′-dimethyl-2,2′-bipyridine) by trivalent polypyridine ML_3^{3+} complexes. Quenching rate constants k_q were obtained from lifetime measurements[3] in 0.5 M sulfuric acid at 25 °C in deaerated solutions. Quenching in these systems is ascribed to an electron-transfer process (eq 2)

$$^*RuL_3^{2+} + ML_3^{3+} \xrightarrow{k_q} RuL_3^{3+} + ML_3^{2+} \tag{2}$$

in which the RuL_3^{2+} excited state, a very strong reducing agent (for L = bpy, $E^0 = -0.83$ V;[4] for L = 4,4′-$(CH_3)_2$bpy, $E^0 = -0.94$ V[3]), gives up an electron to the ML_3^{3+} complex ($E^0 = -0.25, +0.82, +1.10, +1.26$ V for $Cr(bpy)_3^{3+}$,[5] $Os(bpy)_3^{3+}$,[6] $Ru(4,4'\text{-}(CH_3)_2bpy)_3^{3+}$,[3] and $Ru(bpy)_3^{3+}$,[3] respectively). The quenching rate constants determined in this study are plotted against the driving force for electron-transfer quenching in Figure 1. For all seven systems studied the quenching rate constants lie near the diffusion-controlled limit which is (3–4) × 10^9 M^{-1} s^{-1} for reactants of this typeat 25 °C and 0.5 M ionic strength.[3,7] The first three points show a small increase in rate constant as K_{12} for electron-transfer quenching increases. At larger K_{12} values, however, the rate constants *decrease* with increasing driving force. The behavior observed in Figure 1 is thus in qualitative agreement with the predictions of Marcus theory.

We now examine in greater detail the evidence for this conclusion. Bolletta et al. demonstrated that $Cr(bpy)_3^{3+}$ quenching of $^*Ru(bpy)_3^{2+}$ does not proceed by an energy-transfer process[8] and Ballardini et al. have used a flash-photolysis technique to detect the electron-transfer products, $Cr(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$, formed from quenching according to eq 2.[9] Thus this electron-transfer quenching mechanism is firmly established for the $Cr(bpy)_3^{3+}$/$^*Ru(bpy)_3^{2+}$ (and, by analogy, for the $Cr(bpy)_3^{3+}$/$^*Ru(4,4'\text{-}(CH_3)_2bpy)_3^{2+}$) system. Next, the self-exchange rates for the ML_3^{3+} oxidants used are very similar: for the $Cr(bpy)_3^{3+}/Cr(bpy)_3^{2+}$ couple $k_{11} \sim 10^8$ M^{-1} s^{-1} at 25 °C