Communications to the Editor

Protonation of Phthalic Acid: an Unusual Acylium-Carboxonium Rearrangement

Sir:

Protonations of carbonyl compounds have been extensively studied by Olah. Many protonated acids and acyl halides cleave to acylium ions upon temperature elevation. Cyclic and linear aliphatic acid anhydrides cleave asymmetrically upon protonation to the corresponding acylium ion and protonated carboxyl function. However, aromatic acid anhydrides were reported to undergo only diprotonation, without cleavage, and no satisfactory explanation was given to this anomaly. We report the protonation of benzene dicarboxylic acids and their cleavage in magic acid-SO2 to the corresponding acylium ions. We submit that diprotonated phthalic acid \( \text{(Ic)} \) cleaves to a stable species \( \text{2c} \) (or \( \text{2c}' \)) in which, unlike \( \text{2a} \) and \( \text{2b} \), 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-SO2 at \(-30^\circ\text{C}\) the corresponding doubly protonated species, viz., \( \text{1a} \) and \( \text{1b} \), respectively (Table I). Heating of \( \text{1a} \) and \( \text{1b} \) to \(+30^\circ\text{C}\) for several minutes revealed additional sets of bands in the \( ^1\text{H} \) NMR spectra (Table I), which are assigned to \( \text{2a} \) and \( \text{2b} \), i.e., benzene rings bearing an acylium ion and a protonated carboxyl group. The ratios \( \text{1a} : \text{2a} \) and \( \text{1b} : \text{2b} \) are approximately 3:2. When phthalic acid was transformed to the doubly protonated species \( \text{1c} \) (Table I), the \( \text{OH}^+ \) band was observed only below \(-50^\circ\text{C}\) and even then it was relatively broad. The exceptional behavior of the ortho substituted diprotonated species \( \text{2c} \) is analogous to the behavior of protonated dimethyl phthalate. It has already been pointed out that the two carbonyls are close together with both protons mutually bonded. Heating \( \text{1c} \) for a few minutes produced a new set of bands at \(-30^\circ\text{C}\) (Table I). Contrary to \( \text{1a} \) and \( \text{1b} \), the bands of \( \text{1c} \), have completely disappeared. No \( \text{OH}^+ \) absorption was observed even at \(-100^\circ\text{C}\). The symmetry of this spectrum (AA'BB' pattern) can be rationalized prima facie either by the formation of a diprotonated anhydride, viz., \( \text{3} \) or a diacylium ion. The same \( ^1\text{H} \) NMR spectrum is obtained when phthalic anhydride

![Diagram](image)

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

<table>
<thead>
<tr>
<th>Acid</th>
<th>(^1\text{H NMR})a,d</th>
<th>(^1\text{C NMR})e,d,f</th>
<th>(^1\text{H NMR})g,e</th>
<th>(^1\text{C NMR})g,e,f,j</th>
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<tbody>
<tr>
<td>(a) Terephthalic acid</td>
<td>8.68 (s, 4 H, arom) 12.77 (s, 4 H, OH(^+))</td>
<td>127.9 (1), 131.5 (2), 179.4 (carbonyl)</td>
<td>9.81, 9.17 (AA'BB', 4 H, arom) 13.36 (s, 2 H, OH(^+))</td>
<td>99.4 (1), 146.3 (2), 133.9 (3), 140.8 (4), 147.2 (carbonyl), 178.1 (carbonyl)</td>
</tr>
<tr>
<td>(b) Isophthalic acid</td>
<td>8.36, 9.00 (A,B, 3 H), 9.30 (s, 1 H), 12.54 (s, 4 H, OH(^+))</td>
<td>121.0 (1), 134.9 (2), 140.9 (4), 130.9 (5), 178.0 (carbonyl)</td>
<td>8.57, 9.42 (A,B, 3 H, arom), 9.74 (s, 1 H) 13.84 (s, 2 H, OH(^+))</td>
<td>92.8 (1), 148.2 (2), 123.7 (3), 143.4 (4), 133.2 (5), 147.4 (6), 176.0 (carbonyl), 158.5 (carbonyl)</td>
</tr>
<tr>
<td>(c) Phthalic acid</td>
<td>8.48 (s, 4 H, arom), 13.34 (s, 4 H, OH(^+))</td>
<td>120.7 (1), 133.6 (3), 138.0 (4), 181.0 (carbonyl)</td>
<td>8.82 (m, 2 H, arom), 9.20 (m, 2 H, arom)</td>
<td>118.6 (1), 134.5 (3), 140.7 (5), 164.7 (carbonyl)</td>
</tr>
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</table>

\[ a \] 0.1 M solution in a 1:1 v/v SO2:magic acid in sealed NMR tubes. \[ d \] At 100 MHz, Varian HA 100D spectrometer, in ppm relative to hexamethylsiloxane. \[ e \] At 20 MHz, Varian CFT-20, in ppm relative to tetramethysilane; acetone-\( d_6 \) in a capillary served for locking, carbonyl absorption at 204.3 ppm relative to Me2Si was used for calibration. \[ f \] At \(-30^\circ\text{C}\). \[ g \] Sample heated for several minutes to \(+30^\circ\text{C}\). \[ h \] Numbers in parentheses refer to the corresponding carbon atom. \[ i \] Below \(-50^\circ\text{C}\).
reacts at -70 °C with magic acid-SO_2. Formation of a dia-
cyclium 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 for-
mation of diprotonated phthalhydride 3.3

An insight into system 2c, is obtained from its 1^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 mi-
gration (in the NMR scale) of a molecule of water occurs be-
tween the two adjacent carbonyls of 2c. This fast rearrange-
moment occurs either in the following process: 2c = d = 5 = 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 acyl--carboxonium rearrangement 2c → 2c'
is preferred.

References and Notes

Bouis, ibid., 38, 1415 (1973); D. A. Tomalia, ibid., 34, 2583 (1969); J. O. Knoebel 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,
(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 = 2a + H_2O and 1b = 2b + H_2O is involved. In neat magic acid the ratios of 1a:2a and 1b:2b are 2.3, re-
spectively.
(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 anhy-
drides.
(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 re-
actions predicts that a plot of log k_{12} (K_{12}, the rate constant
for the electron-transfer reaction) vs. ΔG^*_{12} (the free energy
change for the electron-transfer reaction) for constant reor-
ganization energy should be parabolic. One remarkable feature
of the theory is the so-called “inverted” region; when -ΔG^*_{12}
> 2(ΔG^*_{11} + ΔG^*_{22}) 2 the intrinsic electron-transfer barrier, the reaction rate constant
should decrease as the free energy change becomes more fa-

vorable. When k_{12} is calculated from eq \ref{eq:11}

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

(\text{where k}_{11} \text{ and k}_{22} \text{ are the self-exchange rates for the oxidizing
and reducing couples, respectively, K}_{12} \text{ is the equilibrium con-
stant for the cross-reaction, and } Z \text{ is a collision number usually
taken as } 10^{11} \text{ M}^{-1} \text{ s}^{-1} \text{, the point of crossover into the inver-
ted region may be expressed as (eq 1c)}

\[ \log K_{12} = 2 \log (Z/k_{11}k_{22}) \] (1c)

It is apparent from condition 1c that crossover into the inver-
ted region is favored when both K_{12} and k_{11}k_{22} are large. Few
opportunities for systematic exploration of the inverted region
exist when both reactants are in their ground electronic states
since K_{12} is not sufficiently large. On the other hand, ex-
cited state systems with small reorganization energies pro-
vide 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 ΔG^*_{12} = -10 to -62 kcal mol^{-1} even though onset of
the inverted region is expected at ΔG^*_{12} = -15 kcal mol^{-1}.
In the present study we have used inorganic oxidants with small
reorganization energies to quench the luminescence of poly-
pyridineruthenium(II) complexes. For this series with k_{11}k_{22} 
~ 10^{16} M^{-2} s^{-2} (ΔG^*_{11} + ΔG^*_{22} \approx 8 kcal mol^{-1}) and
ΔG^*_{12} = 10 to 46 kcal mol^{-1} (inversion predicted at -ΔG^*_{12}
> 16 kcal mol^{-1}) we do find evidence for diminished rate con-
stants in the inverted region.

We have studied the quenching of the luminescence of the
charge-transfer excited states of two polypyridineruthenui-
num(II) complexes RuL_3^{3+} (L = 2,2'-bipyridine or 4,4'-di-
methyl-2,2'-bipyridine) by trivalent polyphenyl ML_3^{3+}
complexes. Quenching rate constants k_{1i} were obtained from
lifetime measurements 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)

\[ \text{RuL}_3^{3+} + \text{ML}_3^{3+} \rightarrow \text{RuL}_3^{3+} + \text{ML}_3^{2+} \] (2)

in which the RuL_3^{3+} excited state, a very strong reducing agent
for L = bpy, E^0 = -0.83 V; for L = 4,4'-(CH_3)_2bpy, E^0 =
-0.94 V, 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+}, Os(bpy)_3^{3+},
Ru(4,4'-(CH_3)_2bpy)_3^{3+}, and Ru(bpy)_3^{2+}; 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^{10} M^{-1} s^{-1} for reactants of this type 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 in-
creases. At larger K_{12} values, however, the rate constants de-
crease 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^{2+}
quenching of \text{Ru(bpy)_3}^{2+} does not proceed by an energy-
transfer process and Ballarini et al. have used a flash-pho-
tolysis technique to detect the electron-transfer products,
Cr(bpy)_3^{2+} and Ru(bpy)_3^{3+}, formed from quenching ac-
cording to eq 2,9 Thus this electron-transfer quenching
mechanism is firmly established for the Cr(bpy)_3^{3+}/
\text{Ru(bpy)_3}^{2+} (and, by analogy, for the Cr(bpy)_3^{3+}/
\text{Ru(4,4'-(CH_3)_2bpy)_3}^{2+}) system. Next, the self-exchange
rates for the \text{ML}_3^{3+} oxidants used are very similar: for the
Cr(bpy)_3^{3+}/Cr(bpy)_3^{2+} couple k_{11} \approx 10^8 M^{-1} s^{-1} at 25 °C

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