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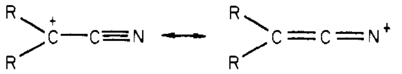
Significant Mesomeric Nitrenium Ion Character of the Cyanodiphenylmethyl Cation, the First Long-Lived Cyanocarbenium Ion[1]

Sir:

Nitrenium ions containing divalent positive nitrogen have been postulated as intermediates in rearrangement, synthesis, and cleavage of nitrogen-containing organic compounds.[2,3] Evidence for their existence as distinct species under stable ion conditions has been negative so far.[4] Attempted generation of nitrenium ions by protonating nitrosobenzenes resulted only in iminium-benzenium dications.[4,5] In principle, a cyano-substituted carbocation (**1a**) in its mesomeric form represents a nitrenium ion



1a 1b

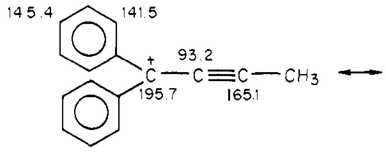
(**1b**), and this aspect has been considered recently in the solvolytic studies of α-cyano tosylates by Gassman and Talley.[6] The solvolytic study[6] of 1-cyano-1-octyl tosylate and 7-cyano-7-norbornadienyl tosylate indicated that the extent of mesomeric nitrenium ion character in the ions depended on the nature of the additional substituents on the cationic center.

We report now the preparation and ^{1}H, ^{13}C, and ^{15}N NMR spectroscopic observation of the cyanodiphenylmethyl cation **1**-C_6H_5 in FSO_3H/SO_2ClF solution. Careful addition of a solution of benzophenone cyanohydrin[7] in SO_2ClF to a tenfold excess of FSO_3H in SO_2ClF at −78°C resulted in a deep orange solution. The ^{1}H NMR spectrum of the solution showed an aromatic multiplet at γ 7.6–8.6 which is significantly deshielded over that in the neutral precursor ($\approx$1 ppm; see Table I). In the ^{13}C NMR spectrum, the cationic carbon absorption was observed at δ 168.8 followed by a para carbon signal at δ 153.3. The cyano carbon absorbed at δ 112.1, about 9 ppm shielded over that in the neutral precursor. The substantial deshielding of both ortho and para carbons and the significant shielding of the cyano carbon are indicative of extensive charge delocalization into the aromatic ring as well as into the cyano group through the mesomeric nitrenium ion form. The cation **1**-C_6H_5 is comparable to the related 1,1-diphenyl-2-butynyl cation **2**[8] (which also has significant mesomeric vinyl cation contribution) although the charge delocalization into the aromatic ring is considerably less in the latter.

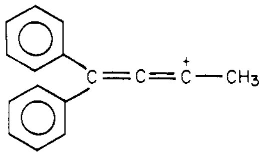
Table I. ^{1}H, ^{13}C, and ^{15}N NMR Data of Cyanodiphenylcarbenium Ion 1-C_6H_5 and Its Progenitor Benzophenone Cyanohydrin

substrate	^{1}H, δ^a	^{13}C, δ^a	^{15}N, δ^b
1-C_6H_5^{c}	7.6–8.6 (m)	C_α^+ = 168.8, C_p = 153.3, C_o, C_o' = 148.2, 143.8, C_m = 133.7, $-C{\equiv}N$ = 112.1	283.0
cyanohydrin^d	7–7.6 (m, 10 H, aromatic), 6.8 (s, 1 H, OH)	C_i = 142.5, C_o, C_p = 128.7, C_m = 125.9, $-C{\equiv}N$ = 125.9, C_α = 75.1	253.0

[a] ^{1}H and ^{13}C NMR chemical shifts are in ppm from external capillary tetramethylsilane. [b] ^{15}N NMR chemical shifts are in ppm from external anhydrous ammonia. [c] In FSO_3H/SO_2ClF solution at −90 °C. [d] In $CDCl_3$ solution at 37 °C.



2a



2b

To ascertain the extent of mesomeric nitrenium ion character in **1**-C_6H_5, we prepared the 10% ^{15}N-enriched ion from the ^{15}N-enriched cyanohydrin precursor.[9] In the ^{15}N NMR spectrum, the cyano nitrogen was observed as a singlet (with no proton coupling) at δ 283.0, which is 30 ppm deshielded over that in the neutral precursor (δ 253.0). The lack of any proton coupling with the nitrogen clearly supports the formation of cyanodiphenylmethyl cation **1**-C_6H_5 and rules out any additional protonation on nitrogen. In fact, a substantial ^{15}N shielding is observed for nitrilium ions ($RC{\equiv}NH^+$) over the neutral nitrile precursor[10] (ca. 100 ppm). The observed 30-ppm deshielding clearly indicates carbon–nitrogen double-bond character. In fact, the ^{15}N chemical shift is more comparable to that of an imine (around δ 318).[10] The observed ^{15}N chemical shift data clearly support substantial mesomeric nitrenium ion contribution to the overall structure of the cation **1**-C_6H_5, in spite of competitive aryl ring delocalization.

Attempts to prepare analogous 1-cyano-1-cyclopentyl, 9-cyano-9-fluorenyl, 1-cyano-1-phenethyl, and 2-cyano-2-norbornyl cations from their corresponding cyanohydrins[7] under a variety of superacidic conditions were, however, unsuccessful. They indicated the formation of respective protonated carbonyl compounds along with a complex mixture of byproducts. We are continuing our studies of the elusive nitrenium ions under stable ion conditions.

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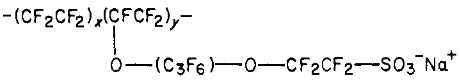
Polymer Films on Electrodes. 4. Nafion-Coated Electrodes and Electrogenerated Chemiluminescence of Surface-Attached Ru(bpy)$_3^{2+}$

Sir:

A pyrolytic graphite electrode coated with the perfluorinated ion-exchange polymer Nafion (**1**)[1] and containing Ru(bpy)$_3^{2+}$ (bpy = 2,2′-bipyridine) was prepared. Electrogenerated chemiluminescence at the polymer layer is produced upon oxidation of the 2+ Ru species in the presence of oxalate ion.



$$-(CF_2CF_2)_x(CFCF_2)_y- \quad | \quad O-(C_3F_6)-O-CF_2CF_2-SO_3^-Na^+$$

1

Electroactive groups can be bound quite readily to an electrode surface in the form of a polymer layer,[2-4] where either the polymer itself is electroactive [e.g., poly(vinylferrocene)][2a] or the electroactive molecules are later attached into the polymer [e.g., Ru(NH$_3$)$_6^{2+}$ on polyacrylic acid].[4b,c] In the latter example, Oyama and Anson demonstrated that ions from solution could be bound to the polymer by exploiting its ion-exchange properties (electrostatic binding).[4c]

Nafion (**1**), an ion-exchange polymer which is very resistant to chemical attack, even by strong oxidants at elevated temperatures, has found increasing use as a membrane material. We have found that a pyrolytic graphite (PG) electrode can be coated with this material. In a typical experiment, a layer of ~1.4 mg of Nafion polymer/cm^2 of electrode surface was prepared by dip coating. The electrode was dipped into a solution of ~2% Nafion (equiv wt ~970) in ethanol, then taken out and dried in the air, leaving the polymer film on the surface. The film thickness can be estimated by using the density of dry commercial Nafion membranes (~2 g cm^{-3}) as ~7 μm (dry). The polymer-coated electrode was then immersed for 10–15 min in a solution of 5 mM Ru(bpy)$_3$Cl$_2$ in 0.1 M H$_2$SO$_4$, rinsed thoroughly with distilled water, and transferred to the electrochemical cell. Electrodes prepared in this manner acquire a deep orange color, demonstrating the large amount of Ru(bpy)$_3^{2+}$ incorporated into the polymer.

Such an electrode, denoted as PG/Nafion, Ru(bpy)$_3^{2+}$, shows the cyclic voltammetric behavior characteristic of the Ru(bpy)$_3^{3+/2+}$ couple when immersed in a solution containing only supporting electrolyte (Figure 1a). However, the observed oxidation and reduction peaks are broad and separated by 170 mV at this scan rate, markedly deviating from the expected behavior of a surface-confined electroactive species.[2a,5a] Such deviations are caused by limitations in the overall rate of the redox process by mass transfer within the film, charge transfer at the substrate/film interface, and associated chemical reactions of the electroactive forms, as well as by nonidealities in the film structure.[2,3,4a,5b] For these films, the peak currents, measured over a range of scan rates (v) of 0.01–1 V/s, were proportional to $v^{1/2}$, indicating that the current was controlled by diffusion in these thick polymer layers.[2a,3b]

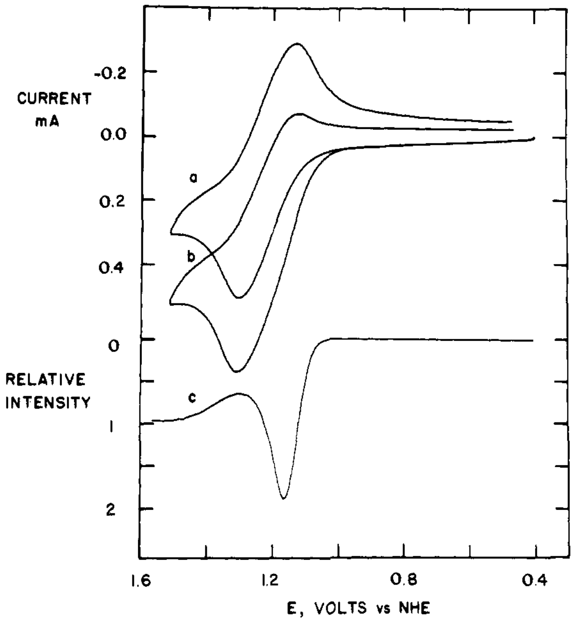


Figure 1. (a) Current–potential curve (sweep rate, 0.1 V/s) for a PG/Nafion, Ru(bpy)$_3^{2+}$ electrode in 0.2 M Na$_2$SO$_4$. (b) Same as (a), with addition of 50 mM Na$_2$C$_2$O$_4$. (c) ecl intensity vs. potential, in the same solution as (b) (anodic scan only). The electrode was a PG (Union Carbide Corp.) cylinder, 0.5-cm diameter, with the basal plane as the active surface.

The amount of Ru(bpy)$_3^{2+}$ attached to the surface was determined by first oxidizing the film at +1.60 V, and then determining the charge required to reduce the film when the potential was stepped to +0.60 V until the current dropped to zero (several minutes). For typical films, the surface concentration of Ru(bpy)$_3^{2+}$ is $(2-4) \times 10^{-6}$ mol/cm^2.

The behavior of the same electrode in an aqueous solution containing 50 mM sodium oxalate is shown in Figure 1b. In the absence of Ru(bpy)$_3^{2+}$ on the Nafion-coated electrode, oxalate itself is oxidized at potentials more positive than Ru(bpy)$_3^{2+}$. However, on the modified electrode, oxalate is catalytically oxidized by the Ru(bpy)$_3^{3+}$ attached to the surface. This is clearly seen in Figure 1b by the increase in the anodic peak current and decrease in the cathodic peak current, caused by the reaction of Ru(III) with C$_2$O$_4^{2-}$. Basically, the same catalysis is also observed when a solution containing Ru(bpy)$_3^{2+}$ and C$_2$O$_4^{2-}$ is oxidized on Pt or carbon electrodes in aqueous solution.[6]

When the potential of a PG/Nafion, Ru(bpy)$_3^{2+}$ electrode in an aqueous solution containing 50 mM Na$_2$C$_2$O$_4$ and 0.2 M Na$_2$SO$_4$ (pH ~6) is stepped to +1.4 V, a constant, very intense orange luminescence is observed, clearly visible to the non-dark-adapted eye. The ecl intensity upon scanning the potential in the positive direction is shown in Figure 1c. The detailed shape of the intensity–potential and intensity–time curves is currently under further investigation. The ecl spectrum is identical with the known luminescence spectrum of Ru(bpy)$_3^{2+*}$.[6,7] The mechanism of the ecl reaction is very likely the same as that previously proposed for the simultaneous oxidation of dissolved

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