Supplementary Material Available: Infrared and proton magnetic resonance spectra, optical rotations, physical constants, thin-layer chromatographic mobility, and elemental combustion analyses of compounds **2**, **4–14**, and isolated intermediates (6 pages). Ordering information is given on any current masthead page.

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(14) Upjohn Predoctoral Research Fellow, 1979–1980.

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First Successful ENDOR Studies of Organic Radical Ions in Liquid Crystals

Sir:

The use of liquid crystalline solvents in ENDOR investigations of organic free radicals has proved to give valuable information about anisotropic hyperfine contributions and quadrupole splittings.[1-4] It has to be pointed out, however, that these studies have been restricted to neutral radicals, owing to the low solubility of ionic species in these nonpolar solvents. Until now very few papers exist that deal only with ESR of radical ions in liquid crystals.[5-10] In the present communication, we report on the generation and ENDOR investigation of semiquinone and semidione type radical anions in nematic and smectic phases. To the best of our knowledge, these are the first successful ENDOR experiments on ionic organic radicals in liquid crystals.

The solubility problem might be overcome by using ionophores such as crown ethers to solubilize ions by complexing the alkali counterion[10,11] or by using lipophilic quaternary ammonium counterions, e.g., in the electrolytic generation of radicals in the presence of relatively large amounts of supporting electrolyte.[6] We could achieve a similar effect by using a quaternary ammonium base in the chemical generation of radical anions. The formation of tight ion pairs might severely affect the results.[10,12] With consideration of that possibility, the use of smectic A phases appeared to be especially advantageous as compared to nematic phases, since both the anisotropic and the isotropic hyperfine interactions are accessible under the same experimental conditions.[13]

The samples were prepared in "nematic phase IV licristal" (nematic phase 289–349 K), in 4-cyano-4′-pentylbiphenyl (5CB, nematic phase 295–308 K), or in 4-cyano-4′-octylbiphenyl (8CB, smectic A phase 294–307 K, nematic phase 307–314 K) as follows: A mixture of anthraquinone and benzoin in the liquid crystal was treated with benzyltrimethylammonium hydroxide or with potassium ethoxide in the presence of dibenzo-18-crown-6 to give anthrasemiquinone radical anion (**1**). Benzil semidione radical anion (**2**) and the respective perdeuterated compound (**3**) were obtained similarly from benzil and benzoin or benzil-d_{10} and benzoin-d_{12}. ESR and ENDOR spectra were recorded on a Bruker ER 220D ESR spectrometer equipped with a Bruker ENDOR cavity (ER 200 ENB) and home-built NMR facilities described elsewhere.[14]

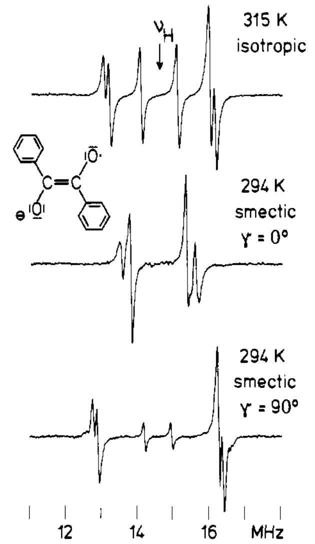

Figure 1. ENDOR spectra of **2** in 8CB, see text.

Table I. Isotropic Proton Hyperfine Coupling Constants and Shifts of 1 (MHz)

	phase IV^a			8CB^b		
position	a_{iso} 354 K	Δa 341 K	Δa 294 K	a_{iso} 315 K	a_{iso} 294 K	Δa 294 K
2,3,6,7	−2.74	+0.48	+0.99	−2.73	−2.73	+0.78
1,4,5,8	−0.91	+0.55	+0.74	−0.89	−0.93	+0.97

^{a} Counterion K$^+$/dibenzo-18-crown-6. ^{b} Counterion benzyltrimethylammonium.

Table II. Isotropic Proton Hyperfine Coupling Constants and Shifts of 2 (MHz)

	5CB			8CB^b		
position	$a_{iso}{}^a$ 315 K	Δa^a 294 K	Δa^b 294 K	a_{iso} 315 K	a_{iso} 294 K	Δa 294 K
p	−3.10	+0.77	+0.65	−3.10	−3.13	+1.09
o	−2.82	+0.85	+0.74	−2.82	−2.83	+1.21
m	+1.02	+0.46	+0.41	+1.03	+1.02	+0.60

^{a} Counterion K$^+$/dibenzo-18-crown-6. ^{b} Counterion benzyltrimethylammonium.

Figure 1 shows the ENDOR spectra of **2** taken in 8CB in the isotropic phase (top) and in the smectic phase at two different angles between the director and the magnetic field.[13] The isotropic hyperfine coupling constants and the shifts are collected in Tables I and II. Our experimental results demonstrate that ENDOR of radical anions can be performed in liquid crystals, that a good signal-to-noise ratio can be achieved, and that the anisotropic hyperfine shifts can accurately be determined from the ENDOR spectra whereas the ESR spectra are poorly resolved. It should be pointed out that the coupling constant shifts are quite large, indicating a high degree of ordering. Actually, the shifts obtained for **1** (Table I) are about five times as large as those reported previously.[7]

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The influence of ion-pair equilibria can be neglected since the hyperfine data are not substantially affected when replacing the potassium/crown ether counterion by benzyltrimethylammonium (Table II). Moreover, the results obtained in 8CB demonstrate that the isotropic hyperfine couplings are not significantly altered when passing from the isotropic to the smectic phase. Consequently, the phase transition is not accompanied by a substantial change in the solvation or the ion-pair structure. It should be noted that the isotropic coupling constants of **2** in liquid crystalline solvents are in agreement with those obtained in dimethylformamide.[15] A similar invariance is found for the large coupling of **1** (−2.73 ± 0.01 MHz, ethanol or toluene), whereas the small coupling is strongly solvent and temperature dependent (−1.53 MHz, ethanol, 210 K; −1.33 MHz, toluene, 210 K; −0.89 MHz, 8CB, 315 K). This probably accounts for the anomalous temperature behavior of the shifts of **1** in "phase IV" (Table I).

Since there is considerable interest in studying quadrupole splittings by means of ENDOR in liquid crystals, it is noteworthy that we succeeded in observing deuterium quadrupole splittings in the ENDOR spectrum of **3**. The splitting amounts to about 160 kHz for the para positions (8CB, 294 K), whereas splittings for the ortho or meta positions could not be resolved.

^{2}H ENDOR quadrupole splittings are strongly dependent on the orientation of the C–D bond, being largest for an orientation parallel to the magnetic field.[3] Therefore, a trans configuration of **3** can be assumed, and the long axes of the molecules are preferentially oriented parallel to the long axes of the solvent molecules. Further ENDOR studies of radical ions in liquid crystals are in progress.

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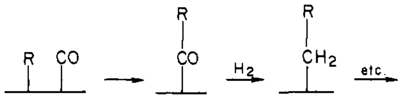
Reactions of Diazomethane on Transition-Metal Surfaces and Their Relationship to the Mechanism of the Fischer–Tropsch Reaction

Sir:

We report results of experiments which are consistent with the original proposal of Fischer and Tropsch made in 1926 that the formation of hydrocarbons produced upon reaction of CO and H_2 on certain transition-metal surfaces (the Fischer–Tropsch reaction) proceeds via "polymerization of methylene groups" on the metal surface.[1] The methylene groups were suggested to arise by reduction with H_2 of carbon atoms formed, following decomposition of CO on the metal.

An alterative mechanism, which subsequently has received widespread acceptance, was one in which the C–C bonds of the product were initially derived from insertion of adsorbed CO molecules into metal–alkyl groups on the surface.[2] Reduction of the acyl group to an alkyl group and repetition of the insertion of CO were proposed to lead to chain growth (eq 1). This proposal



(1)

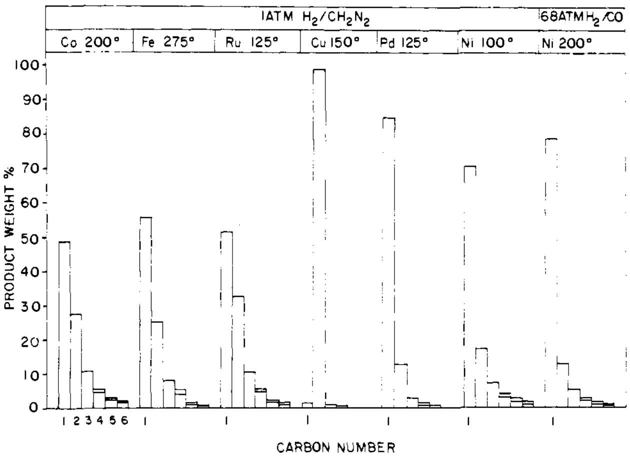


Figure 1. Hydrocarbon product weight distributions over various supported transition metals: saturated and olefinic products are indicated together; the distribution of linear to branched products is indicated by the intermediate line, the linear materials given by the lower section.

derived credibility from the well-established phenomenon in homogeneous organometallic systems of the insertion of CO ligands into metal–alkyl bonds, leading to metal–acyl derivatives.

However, recent studies have confirmed the dissociative chemisorption of CO on single-crystal metal surfaces and strongly implicate the role of this step in the formation of hydrocarbons when H_2 is present.[3]

The nature of the reaction of CO and H_2 over various transition metals varies markedly with the particular metal. Over metals such as Fe, Co, and Ru (Fischer–Tropsch catalysts), there is produced a mixture of hydrocarbons, the exact nature of the product further depending on the particular reaction conditions employed (temperature, pressure, CO/H_2 ratio, flow rate, etc.), but the mixture characteristically consists of linear alkanes and monoolefins with lesser amounts of nonlinear isomers. The components may range from methane to high molecular weight material resembling linear polyethylene. With Ni and Pd, methane is the principal product formed while with Cu there is no reaction.

To answer the question as to how methylene groups would behave on a metal surface, we have examined the products of the reaction of diazomethane (CH_2N_2) with and without H_2 over various transition metals with the expectation that dissociative chemisorption of CH_2N_2 to absorbed methylene groups and N_2 would occur. The gas-phase thermal decomposition of diazomethane at 290–400 °C has previously ben studied and is found to produce mainly CH_4, C_2H_6, C_2H_4, C_2H_2, and HCN; when excess H_2 is present, the products are primarily CH_4 and C_2H_6.[4] The reaction is interpreted in terms of intermediate formation of CH_2 fragments, but significant amounts of polymerization to higher hydrocarbons were not observed.[5]

We find that CH_2N_2,[6] diluted with an inert gas (He or N_2) is rapidly and quantitatively decomposed upon passage over Ni, Pd, Fe, Co, Ru, and Cu surfaces[7] at 1 atmosphere of pressure and in the temperature range 25–200 °C, and in each case ethylene

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(5) The liquid-phase decomposition of ethereal solutions of CH_2N_2 over extended periods (8–24 h) on surfaces such as procelain or on metals such as Cu or Au leads to the formation of polymethylene; see: Nasini, A. G.; Trosserelli, L.; Saini, G. *Makromol. Chem.* **1961**, *44–46*, 550–569.

(6) Typically, a solution of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide in anisole is pumped into a stirring solution of aqueous KOH in 2-(2-ethoxyethoxy)ethanol and the generated diazomethane is swept from the reaction flask with an inert gas through a KOH drying tube. The diluted diazomethane can then be mixed with other gases before entering a heated glass tubular reactor containing the catalyst.

(7) The Fe, Co, and Ni catalysts were obtained from the Harshaw Chemical Co. The Pd, Ru, and Cu catalysts were prepared by deposition of the chloride or nitrate salts from aqueous solution on a support (Cab-O-Sil or kieselguhr). All catalysts were reduced at 400 °C in a stream of H_2.

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