$\rho^+ = -0.59$ (correlation coefficient, $r = 0.997$) and a poorer correlation with σ ($\rho = -0.77$, $r = 0.944$).

Our first scheme for determining k_H values involves thermal homolysis of AIBN in solvent RSH* containing two hydrogen donors, QH and Q^0H. The radicals from the initiator convert a fraction of the thiol to thiyl radicals[7,8,10–12] which abstract hydrogen from QH or Q^0H (eq 1 and 3). The $Q\cdot$ and $Q\cdot^0$ radicals

$$RS\cdot + Q^0H \xrightarrow{k_{H^0}} RSH + Q\cdot^0 \qquad (3)$$

$$Q\cdot^0 + RSH^* \longrightarrow Q^0H^* + RS\cdot \qquad (4)$$

then undergo reactions 2 and 4 and become labeled. Kinetic analysis leads to eq 5, where A_{QH} and A_{Q^0H} are the molar specific activities of the recovered substrates and I and I^0 are the isotope effects k_H/k_T on eq 2 and 4, respectively.[13]

$$k_H/k_{H^0} = (I/I^0)(A_{QH}/A_{Q^0H}) \qquad (5)$$

In the second scheme, triphenyl phosphite (TPP) replaces one of the hydrogen donors.[14]

$$RS\cdot + (PhO)_3P \xrightarrow{k_P} R\cdot + (PhO)_3PS \qquad (6)$$

$$R\cdot + RSH^* \longrightarrow RH^* + RS\cdot \qquad (7)$$

Kinetic analysis yields eq 8, where A_{RSH} is the molar

$$A_{QH}[TPP] = (k_H/k_P)(I^{-1})(A_{RSH})[RH] \qquad (8)$$

specific activity of the thiol and [RH] is the *total* yield of cyclohexane. A plot of A_{QH}[TPP] *vs.* [RH] at constant thiol activity yields a straight line with zero intercept and a slope which is proportional to k_H. Data from such plots for two substrates yield relative k_H values (eq 9).

$$k_H/k_H^0 = (I/I^0)(\text{slope for QH plot})/(\text{slope for } Q^0H \text{ plot}) \qquad (9)$$

The assumptions made in deriving the kinetic expressions, eq 5 and 9, are as follows. (1) [RSH] $\gg$ [RST]. (2) Only a small fraction of the QH becomes labeled. Both requirements 1 and 2 were satisfied in our work. (3) A steady state in the concentration of $Q\cdot$ radicals obtains. (4) Only the listed reactions are involved in the formation of the products studied. This was demonstrated by showing that extensive variation in the reaction variables (including replacing AIBN by *tert*-butyl peroxycyclohexanecarboxylate) does not affect the relative values of k_H.

Controls also were performed in which the value of $(k_H)_A/(k_H)_B$ obtained from direct competition between substrates A and B was compared with the results of two separate cross-competitions, one involving A and C (a third substrate) and another between B and C. These direct and indirect measures of $(k_H)_A/(k_H)_B$ always were in good agreement.

(5) $Q\cdot$ and $Q\cdot^0$ radicals are not involved in termination processes. This was verified for cumyl radicals by detailed product studies using glpc of reaction mixtures similar to those from scheme I in Table I but containing cumene as the only hydrogen donor. The amounts of $C_6H_{11}SC(CH_3)_2Ph$, $C_6H_{11}SCH_2CH(CH_3)Ph$, and bicumyl account for less than 1% of the cumyl radicals formed in a sample. The data also show that the yield of isobutyronitrile was twice that of dicyclohexyl disulfide, indicating that dimerization of the thiyl radicals is the only significant termination reaction occurring in these systems.

Our ρ^+ value of -0.59 can be compared with $\rho^+ = -0.86$ obtained for abstraction by atomic bromine,[15] and $\rho^+ = -0.53$ for abstraction by trichloromethyl radicals[15] (all three ρ values apply to ethylbenzenes at 80°).[16,17] These three ρ values are of interest in the light of the recent novel and ingenious suggestions of Zavitsas.[18–20]

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[17] The original data on addition of thiyl radicals to olefins (see ref 1 pp 216–218) indicated a substantial electrophilic polar character for the radicals. The newer, revised data, however, suggest a much smaller effect, perhaps, as suggested by Kellogg, because the reactions are appreciably exothermic (ref 2a, pp 39–41).

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[20] A. A. Zavitsas, *Chem. Technol.*, **2**, 434 (1972). We thank Professor Zavitsas for allowing us to see preprint copies of ref 19 and 20.

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Photo-CIDNP Detection of Transient Intermediates. The Enol of Acetophenone

Sir:

CIDNP studies are ideally suited to reveal the presence of thermally unstable products of radical reactions.[1] The large intensity enhancements in CIDNP spectra result from polarization in newly formed product molecules (and decay with T_1) so that, unlike most physical techniques, it is the concentration of recently formed species, rather than the total concentration of the species, that is important. We now report an example of this CIDNP application in the detection of the enol formed during the photolysis of acetophenone.

Hydrogen abstraction reactions of the triplet excited state of acetophenone (**1**) have long been known to lead to reductive dimerization of the ketone.[2] Recently,[3] a novel hydrogen abstraction from phenol (**2**) by acetophenone was reported to lead to 1,2-dibenzoylethane (**3**) as well as acetophenone pinacol in high yield. The

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[2] Ch. Weizman, E. D. Bergmann, and Y. Hirshberg, *J. Amer. Chem. Soc.*, **60**, 1530 (1938).

[3] H.-D. Becker, *J. Org. Chem.*, **32**, 2140 (1967). We would like to thank Professor N. J. Turro for bringing this reference to our attention.

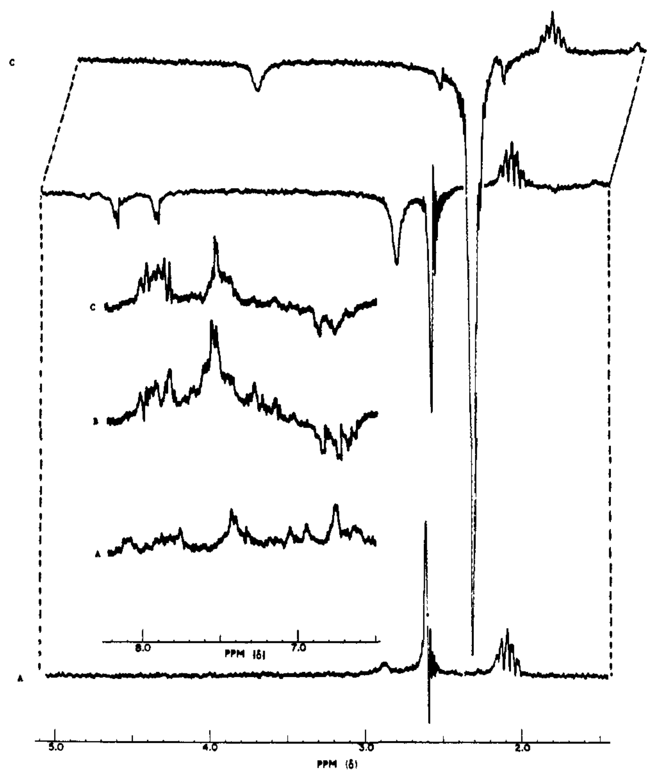
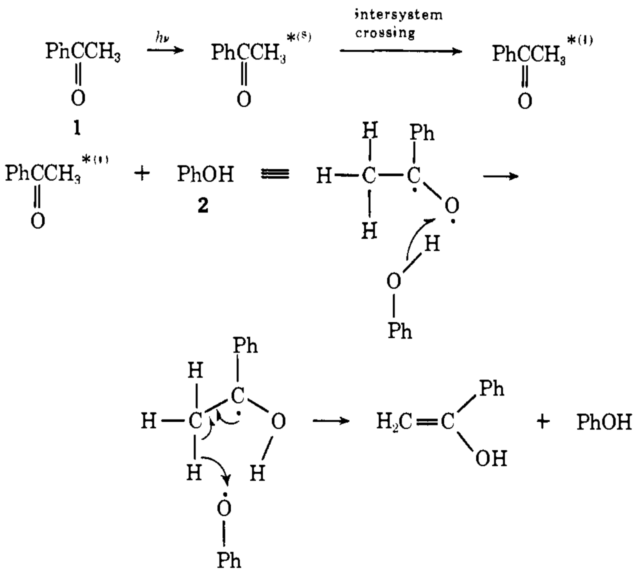


Figure 1. Photolysis of 0.2 *M* acetophenone and 0.05 *M* phenol in acetone-d_6. Spectra recorded (A) before irradiation, (B) during irradiation, and (C) during irradiation of a sample to which 5×10^{-5} *M* *p*-toluenesulfonic acid was added.

author attributed the yield of **3** to hydrogen abstraction by triplet acetophenone from its enol (followed by dimerization of the resulting radicals) and suggested that the enol was formed by the process shown in Scheme I.

Scheme I



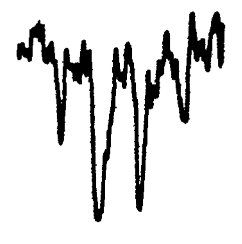
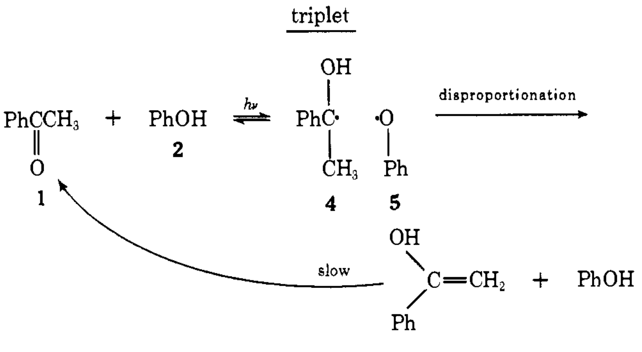


Figure 2. Spectrum recorded during photolysis of 0.2 *M* propiophenone and 0.05 *M* phenol in acetone-d_6.

We have obtained photo-CIDNP results which provide direct evidence for the formation of the enol of **1** and also supply further information on the mechanism of its formation. Photolysis of 0.2 *M* acetophenone and 0.05 *M* phenol in acetone or acetone-d_6 solution with the unfiltered beam of a high-pressure mercury arc lamp inside the modified probe of an HA-60 nmr spectrometer led to the spectrum in Figure 1B. The polarized signals are due to the methyl protons of **1** (δ 2.6, s) and the hydroxyl proton of **2** (δ 2.9, s). The AX quartet (δ 4.5) was assigned to the methylene protons of the enol of **1** by comparison with the spectrum of the methylene protons of the ethyl ether[4] of the enol of **1** (δ 4.22, d; δ 4.55, d, $J = 2.5$ cps). Photolysis of an identical mixture of **1** and **2** in acetone-d_6 but with a trace of *p*-toluenesulfonic acid added showed no enol polarization but showed a stronger emission signal for the methyl protons of **1** (Figure 1C). Likewise, photolysis in *tert*-butyl alcohol-*O-d* led to no enol polarization but, again, a stronger emission from **1**. Photolysis of neat **1** with a trace of phenol also showed emission signals for the enol methylene protons.

Application of the simple rules based on the radical pair model of CIDNP,[1] using literature values[5,6] for the *g* factors and hyperfine splittings of **4** and **5**, demonstrates that a reversible abstraction by triplet acetophenone is consistent with the data (Scheme II).

Scheme II



Photolysis in alcohol solution or in the presence of acid decreases the enol lifetime to the point where it is not observable on the nmr time scale. Under these conditions, the enol polarization simply contributes to the intensity of the polarization of acetophenone. Corresponding polarized signals were also observed in the ring protons of **1** and **2** during photolysis in acetone or acetone-d_6 (Figure 1B: δ 7.9, ortho protons of **1**, enhanced absorption; δ 6.7, ortho protons of **2**, emission).

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(4) H. O. House and V. Kramer, *J. Org. Chem.*, **28**, 3362 (1963).

(5) $g = 2.0031$, by analogy to 1-hydroxypropyl radical: R. O. C. Norman and R. J. Pritchett, *Chem. Ind.* (*London*), 2040 (1965); $a_{\text{CH}_3} \cong +17$: H. Paul and H. Fischer, *Chem. Commun.*, 1038 (1971).

(6) $g = 2.0052$, by analogy to 2,4,6-tri-*tert*-butylphenoxyl radical: J. Wertz, C. F. Koelsch, and J. L. Vivo, *J. Chem. Phys.*, **23**, 2194 (1955); $a_{\text{ortho}} = -6.6$ G, $a_{\text{meta}} = +1.9$ G: B. T. Allen and W. Vanneste, *Nature* (*London*), 991 (1965).

A similar experiment in which propiophenone (**6**) was substituted for **1** led to emission for the methylene protons of **6** and weak enhanced absorption for the methyl protons of **6**. An additional emission signal, shown in Figure 2, was assigned to one or both of the isomeric enols of **6** in analogy to the above results.

The observation of these two enols constitutes the first report[7] of CIDNP signals from a transient intermediate. Since these transients are normally in an equilibrium which greatly favors the parent tautomer, photo-CIDNP provides a unique method of recording their spectral parameters. This, of course, suggests the feasibility of measuring shifts and coupling constants of a wide range of structurally similar enols as a method of examining this important class of intermediates. Similarly, study of the temperature (or acid concentration) dependence of these spectra serves as a probe into the kinetic properties of these highly unstable compounds.

Photolysis of **1** and **2** in benzene leads to an enhancement for the methyl protons of **1** which begins as absorption but soon inverts to emission. The results in this and related systems will be presented in detail elsewhere.

Acknowledgments. This work was supported by grants from the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society.

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(7) G. L. Closs has recently informed us that he also has observed enol formation during ketone photolysis.

(8) Alfred P. Sloan Foundation Research Fellow.

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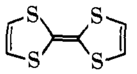
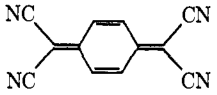
Electron Transfer in a New Highly Conducting Donor–Acceptor Complex

Sir:

Our interest in the synthesis and electron-transfer properties of novel organic,[1] inorganic,[2,3] and organometallic[4] materials has led to the preparation of a new highly conducting complex between the electron donor tetrathiofulvalene (TTF) and the electron acceptor tetracyano-*p*-quinodimethane (TCNQ) in which the TTF/TCNQ ratio is 1 : 1.


TTF


TCNQ

This new compound not only behaves like a metal over a large temperature range but has by far the largest maximum electrical conductivity of any known organic compound ($\sigma_{\max}$ (obsd) = 1.47×10^4 ohm^{-1} cm^{-1} at 66°K).[5]

As a donor, TTF is known to form good electron-conducting cation radical complexes (*e.g.*, $\mathrm{TTF^+Cl^-}$).[6] Similarly, TCNQ forms highly conducting radical anion complexes containing one dimensional conducting chains of face to face stacked TCNQ groups.[7] The electrical conductivity of $\mathrm{TCNQ}\cdot^-$ complexes has been interpreted in terms of a mobility activated electron transfer between a high density of localized states, the localization being induced by either the random orientation potential of the asymmetric cation[8,9] or possibly by defects along the one dimensional chain.[10] Alternatively it has been proposed that electrons are localized by their coulomb correlation and that transport occurs with carrier activation proportional to the coulomb correlation energy (Mott–Hubbard model).[11,12]

The electron transport properties of (TTF)(TCNQ) are thus of interest for several reasons. (a) TTF is highly symmetric (point group D_{2h}) and thus random potentials due to asymmetric orientation are less likely than for other cations previously investigated. (b) TTF is highly polarizable because of the presence of sulfur and thus coulomb repulsion between electrons on neighboring TCNQ sites should be considerably less than suggested for other TCNQ complexes prepared with nitrogen-containing heterocyclic cations of similar size to TTF.[11,12]

TTF was synthesized by deprotonation of 1,3-dithiolium hydrogen sulfate.[13,14] When highly purified TTF and TCNQ are combined in acetonitrile solvent the 1 : 1 complex precipitates from the solution.[15] The ultraviolet spectrum of the complex in hexamethylphosphoramide solvent shows the presence of the TTF radical cation[16] and the TCNQ radical anion.[17] No absorption due to neutral TCNQ is observed. Recrystallization of the complex from dry, deoxygenated acetonitrile provided thin shiny crystal plates with one long axis. The crystals appear black and opaque by reflected light, but when thin sections are viewed under a microscope they appear olive green by transmitted light. Steps and striations run across the plates and easy cleavage parallel to the plate suggests weak interactions between layers. Even when a large excess

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(5) For several crystals the conductivity at 66°K varied from 0.298×10^4 to 1.47×10^4 ohm^{-1} cm^{-1}. It is possible that the conductivity may be even higher if crystals with fewer defects can be produced. The maximum electrical conductivity previously noted for any organic compound was 170–440 ohm^{-1} cm^{-1} at 200°K: A. J. Epstein, S. Etemad, A. F. Garito, and A. J. Heeger, *Phys. Rev. B*, **5**, 952 (1972); L. B. Coleman, J. A. Cohen, A. F. Garito, and A. J. Heeger, to be submitted for publication.

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