resonances obtained of VIII and of the symmetrical coupling product X. Although the tetraphenylethane IX comprises more than 25% of the product, its polarization is too weak to be detectable. The net emission of X must have its origin from sorting in the primary cage since free-radical coupling of two identical species cannot give net polarization ($\Delta g = 0$). The expected polarization of the free-radical-derived symmetrical coupling products IX and X can be calculated from

$$(P_{ij})_{\mathrm{rc}} = (P_{ij})_{\mathrm{rad}} k_{\mathrm{c}}[\mathrm{R}]/(k_{\mathrm{c}}[\mathrm{R}] + 1/(T_1)_{\mathrm{r}}) \qquad (5)$$

where k_c is the rate constant of the coupling reaction and [R] is the steady-state concentration of the radical. From the peak intensities and eq 2 and 5, one finds for the benzyl radical $1/(T_1) \simeq 2k_c[\mathrm{R}]$. From the known radical concentration and the literature value of k_c,[15] $(T_1)_r$ is found to be 3.5×10^{-4} sec. For the *p,p*-dibromobenzhydryl radical $1/(T_1)_r > 12k_c[\mathrm{R}]$, but since its coupling rate is not known, no limit can be set for $(T_1)_r$. Finally, in the reaction of diphenylmethylene with *p*-bromotoluene (X = H; Y = *p*-Br; *m* = 3) none of the symmetrical coupling products shows any measurable polarization. With a known k_c for the dimerization of the benzhydryl radical[16] its relaxation time is calculated to be smaller than 10^{-4} sec. Although the relaxation times thus calculated are somewhat longer than expected from the dipolar relaxation model, the discrepancy is less than a factor of 10 and the comparison of benzyl with benzhydryl relaxation times give the correct ordering. If one assumes $(T_1)_r$ of *p*-bromobenzyl is not much shorter than $(T_1)_r$ of benzyl radical, it follows that the coupling of the bromo-substituted radical is slower than that of its unsubstituted analog. This is in agreement with previous results.[16]

We conclude by observing that there is no need for a mechanism postulating the origin of CIDNP in the free-radical transfer step[17] and note that the radical-pair model accounts for all reported spectra.

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(15) R. D. Burkhart, *J. Amer. Chem. Soc.*, 90, 273 (1968).

(16) S. A. Weiner and G. S. Hammond, *ibid.*, 91, 986 (1969).

(17) The recently postulated mechanism [F. Gerhart and G. Osterman, *Tetrahedron Lett.*, 4705 (1969)] is untenable on chemical grounds because it necessitates three virtually uncoupled electrons and transition state lifetimes of $\sim 10^{-10}$ sec.

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Application of the Radical-Pair Theory of Chemically Induced Dynamic Nuclear Spin Polarization (CIDNP) to Photochemical Reactions of Aromatic Aldehydes and Ketones[1]

Sir:

We wish to report the elucidation of the reaction mechanisms underlying the occurrence of CIDNP in uv-irradiated solutions of aromatic carbonyl compounds.[2] In addition we hope to demonstrate that judicious application of the radical-pair theory of CIDNP[3] can give information going far beyond the obvious conclusion that nuclear-spin-polarized products must have arisen from paramagnetic precursors.

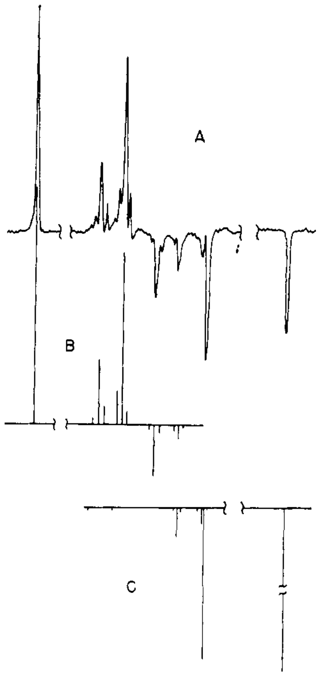

Figure 1. A, CIDNP spectrum of Ib obtained by recording one sweep of irradiated Ib and subtracting one sweep of the dark spectrum of Ib with the aid of a CAT. Field increases from left to right. B and C, calculated CIDNP spectra of Ib and IIb, respectively.

When dilute solutions of benzaldehyde (Ia) and its *p*-chloro (Ib) and *p*-bromo (Ic) derivatives are irradiated, CIDNP is observed for all aldehyde transitions and for signals which can be identified to originate from the corresponding benzoins IIa–c. The spectrum obtained from Ib is shown in Figure 1A. The triplet multiplicity of the precursor of the required pair is established by piperylene quenching which follows a relationship of $I_0/I = y/C_{\mathrm{pip}}$ with $y = 47$ mol/l. for benzaldehyde and where I and I_0 are the intensities of the aldehyde proton transition in the presence and absence of the quenching reagent, respectively.

Inspection of the aromatic proton signal pattern strongly suggests the hydroxybenzyl radical as one of the components (R_1) of the radical pair[4] while the other (R_2) may be either the benzoyl radical or may originate from the solvent *via* hydrogen abstraction. The latter possibility is ruled out by the failure of the signals to respond to a change in solvent from cyclohexane to *p*-bromotoluene, which should have led to a reversal of signs of polarizations because Δg is expected to be of opposite sign in the two systems.[3d,e] Proceeding on the assumption of the intermediacy of the

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(1) Supported by the National Science Foundation (Grant No. GP-18719).

(2) *Cf.* M. Cocivera and A. M. Trozzolo, *J. Amer. Chem. Soc.*, 92, 1772 (1970).

(3) (a) G. L. Closs, *ibid.*, 91, 4552 (1969); (b) G. L. Closs and A. D. Trifunac, *ibid.*, 91, 4554 (1969); (c) R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, 4, 195, 214 (1969); (d) G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, 92, 2183 (1970); (e) G. L. Closs, C. E. Doubleday, and D. R. Paulson, *ibid.*, 92, 2185 (1970); (f) G. L. Closs and A. D. Trifunac, *ibid.*, 92, 2186 (1970); (g) G. L. Closs and A. D. Trifunac, *ibid.*, 92, 7227 (1970).

(4) The nature of the radical is evident from the fact that ortho and para protons are polarized with signs opposite to that of the meta protons, indicating opposite signs of the hyperfine coupling constant. This rules out a σ radical and strongly suggests a benzylic π radical.

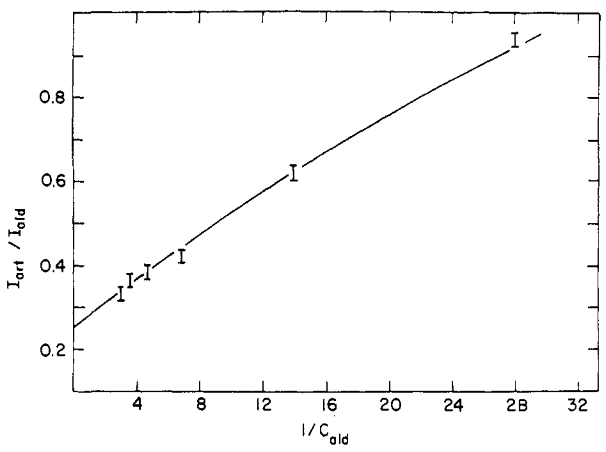
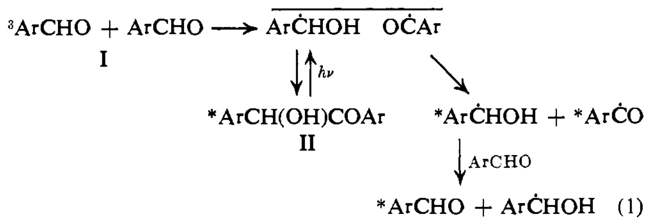


Figure 2. Ratios of the most intense ortho proton and aldehyde proton transitions as a function of inverse aldehyde concentration. The curve presents the function calculated with relaxation times and k_{tr} as given in the text.

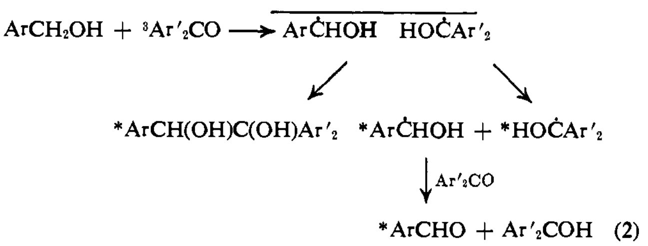
hydroxybenzyl–benzoyl radical pair, measurements of the g factors by conventional esr techniques established $g_1 - g_2 > 0$. This information together with the precursor multiplicity and the known signs of the hyperfine coupling constants eliminate a reversal of the abstraction step as the source of polarized benzaldehyde because polarizations with signs opposite to those observed are expected for this mechanism. This leaves the scheme outlined in (1): benzoin is formed by cage collapse and the escaping free radicals are polarized oppositely to the cage product.[3g] On encounter with benzaldehyde the hydroxybenzyl radical transfers a hydrogen atom to give polarized benzaldehyde and unpolarized hydroxybenzyl radicals.[5]



$$^3\mathrm{ArCHO} + \mathrm{ArCHO} \longrightarrow \overline{\mathrm{Ar\dot{C}HOH\quad O\dot{C}Ar}}$$
$$\mathrm{I}$$
$$\overline{\mathrm{Ar\dot{C}HOH\quad O\dot{C}Ar}} \underset{h\nu}{\rightleftarrows} {}^*\mathrm{ArCH(OH)COAr}\ (\mathrm{II})$$
$$\overline{\mathrm{Ar\dot{C}HOH\quad O\dot{C}Ar}} \searrow {}^*\mathrm{Ar\dot{C}HOH} + {}^*\mathrm{Ar\dot{C}O} \xrightarrow{\mathrm{ArCHO}} {}^*\mathrm{ArCHO} + \mathrm{Ar\dot{C}HOH} \quad (1)$$

* denotes polarized product

This scheme is confirmed by several additional observations. When benzaldehyde is produced by dehydrogenation of benzyl alcohol with photoexcited benzophenone, no net polarization is observed because Δg of the radical pair is ~ 0. With p,p-dibromobenzophenone, however, the aldehyde is strongly polarized with the opposite sign as in the direct irradiation of benzaldehyde. This reversal is expected if a radical pair with $\Delta g < 0$ is the origin of hydroxybenzyl radical as shown in (2). The most convincing evidence is derived from relaxation effects in the hydroxybenzyl radical. Because of different electron–proton dipolar interactions the nuclear relaxation times should not be identical for different protons. Consequently, the relative intensities of the various signals in a product derived from free radicals is a function of the radical lifetime which, in the case at hand, depends on the aldehyde concentration.[3g] The ratio of the signal intensities of ortho and aldehyde protons is given by



$$\mathrm{ArCH_2OH} + {}^3\mathrm{Ar'_2CO} \longrightarrow \overline{\mathrm{Ar\dot{C}HOH\quad HO\dot{C}Ar'_2}}$$
$$\overline{\mathrm{Ar\dot{C}HOH\quad HO\dot{C}Ar'_2}} \swarrow {}^*\mathrm{ArCH(OH)C(OH)Ar'_2}$$
$$\overline{\mathrm{Ar\dot{C}HOH\quad HO\dot{C}Ar'_2}} \searrow {}^*\mathrm{Ar\dot{C}HOH} + {}^*\mathrm{HO\dot{C}Ar'_2} \xrightarrow{\mathrm{Ar'_2CO}} {}^*\mathrm{ArCHO} + \mathrm{Ar'_2COH} \quad (2)$$

$$I_o/I_{ald} = \frac{(P_o)_r[k_{tr}C_{ald} + 1/(T_{benz})_r](T_o)_d}{(P_{benz})_r[k_{tr}C_{ald} + 1/(T_o)_r](T_{ald})_d}$$

where $(P)_r$ is the polarization of the radical when formed, k_{tr} is the transfer rate constant, $(T)_r$ and $(T)_d$ are the nuclear longitudinal relaxation times in the radical and diamagnetic product, respectively, and the subscripts denote the proton positions in the radical and product.[6] Figure 2 shows the intensity ratios of the most intense ortho line and the aldehyde line as a function of the inverse of concentration. Extrapolation to infinite concentration gives the value 0.25, in excellent agreement with 0.28 as calculated from esr parameters and the experimentally measured diamagnetic relaxation times. The curvature and the steepness of the function relate the two radical relaxation times and k_{tr}. Assuming $(T_{benz})_r = 10^{-4}$ sec[7] and using the experimental intercept, the best fit is obtained with $(T_o)_r = 1.5 \times 10^{-3}$ sec and $k_{tr} = 8 \times 10^4$ l. M^{-1} sec^{-1}. Figures 1B and 1C show the calculated spectra of Ib and IIb as computed from experimental esr and nmr parameters including relaxation times.[8] Comparison with Figure 1A shows excellent agreement.[9]

Irradiation of acetophenones in cyclohexane gives polarized spectra in which the methyl group of the ketone emits. A similar analysis shows that the mechanism is essentially the same as that established for benzaldehyde except that the radical pair is derived from solvent abstraction. This was shown by g-factor variation of the solvent leading to an inversion of the polarization with added p,p-dibromodiphenylmethane.

Type I cleavage was observed with benzoin which gives the same radical pair and the identical spectra as irradiated benzaldehyde. Similarly, deoxybenzoin upon irradiation shows a strong emission line of its benzyl protons, indicating the partial collapse of the initially formed radical pair to re-form the starting material. Although only a small fraction of the

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(5) A similar hydrogen transfer has been suggested by J. N. Pitts, Jr., R. Letsinger, R. Taylor, S. Patterson, G. Recktenwald, and R. Martin, *J. Amer. Chem. Soc.*, **81**, 1068 (1959).

(6) This equation follows from eq 4, ref 3g.

(7) This value has been chosen to be somewhat smaller that the benzylic protons in benzyl radical[3] because the rotational correlation time of the p-chlorohydroxybenzyl radical should be somewhat longer.

(8) (a) A computer program has been written which is based on LAOCOON II. A population analysis has been added for each energy level according to equations given in ref 3d–g. (b) Esr parameter used: R_1, $A_{benz} = -14.7$, $A_o = -5.0$, $A_m = 1.25$ G; R_2, $A_o = 0$, $A_m = 1.2$ G; $\Delta g = 3 \times 10^{-3}$; exchange coupling constant $= 10^8$ rad/sec; lifetime of radical pair $= 3 \times 10^{-10}$ sec.

(9) No corrections have been made for the diamagnetic relaxation times in IIb. Therefore, a direct comparison of the relative intensities of the benzylic with the aromatic proton transitions appears to give a calculated value too large for the benzylic proton line, $(T_{benz})_d < (T_{arom})_d$.

radical pairs returns to starting material,[10] this may be considered evidence for a nonradiative decay of the state *via* a bond-breaking and re-forming process.

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(10) According to the calculated electron spin correlation time,[3c] this should be less than 1%.

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Photoelectron Spectroscopy of Organic Ions. I. Carbon 1s Electron Binding Energies of the *tert*-Butyl, Trityl, and Tropylium Cations

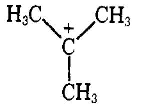
Sir:

Direct measurements of carbon 1s electron binding energies in several hydrocarbons by means of the recently developed X-ray photoelectron spectroscopy[1] yielded a rather narrow range of chemical shifts.[2] For instance, one cannot make a distinction between the carbon atoms of neopentane and those of benzene because their 1s binding energies are virtually the same (290.4 eV). Ethane (290.6), ethylene (290.7), and acetylene (291.2 eV) carbon 1s binding energy differences are well below the presently attainable resolution.[3] These results are in agreement with theoretical expectations. Core electrons are barely affected unless their screening against nuclear attraction is modified by a significant change in the outer (valence) electron shell. In other words, core electron binding energies are mainly dependent on the formal charge of the corresponding atom and on the electronegativity of attached atoms or groups of atoms. The fact that such factors are minimal in hydrocarbons accounts for the small differences described above.

However, X-ray photoelectron spectroscopy should be particularly useful for the investigation of the corresponding ions. Within such molecules the formal charge is generally unequally shared by different atoms. Consequently, the core electrons of these atoms are differently screened and show increasing binding energies with increasing positive charge localization. In the latter cases, the energy differences should be large enough to give rise to separate K-shell photoelectron lines.

We wish now to report the first soft X-ray photoelectron spectra of carbenium ions obtained in frozen superacid solutions or as isolated salts. To illustrate the potential and limitations of the method, we have chosen two types of ions: the *tert*-butyl cation (**1**) (with charge localization) and the trityl (**2**) and tropylium (**3**) cations (with charge delocalization).

The *tert*-butyl cation was generated at −78° from *tert*-butyl chloride in a 1:1 (v/v) SbF_5–SO_2 solution.[4]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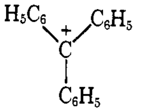
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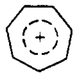
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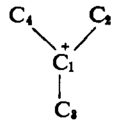
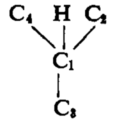
Sulfur dioxide was subsequently removed by the usual freeze–thaw procedure. A thin layer of the viscous SbF_5 solution was deposited on the precooled sample holder, in a dry nitrogen atmosphere. The spectrum was recorded at liquid nitrogen temperature.[5]

Table I. *Ab Initio* and Experimental Data for *tert*-Butyl Cation and Isobutane

	Calcd E_b		Exptl E_b		Calcd ΔE_b	Exptl ΔE_b	Calcd charge	
Compd	C_1	C_2, C_3, C_4	C_1	C_2, C_3, C_4	$(C_1 - C_2)$	$(C_1 - C_2)$	C_1	C_2, C_3, C_4
	312.06	307.61	288.6	285.2	4.45	3.4	+0.328	−0.216
	300.52	300.11	283.9		0.41	<0.5	−0.014	−0.176

The binding energies E_b (defined as differences between the Fermi level and the 1s atomic level energies) are given by the equation

$$E_b = E_{h\nu} - E_k - \Phi_s$$

where $E_{h\nu}$ is the energy (1485.6 eV) of the exciting radiation (Al Kα X-rays), E_k is the measured kinetic energy of the photoejected electron, and Φ_s (= 4.6 eV) is the spectrometer work function (the energy necessary to bring the electron from the Fermi level to the free-electron level). The analyzer energy was 30 eV. The photoelectron spectrum of *tert*-butyl cation (Figure

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(1) (a) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren, and B. Lindberg, "ESCA, Atomic, Molecular, and Solid State Structure Studies by Means of Electron Spectroscopy," Almquist and Wiksells Boktryckeri, AB, Uppsala, 1967; (b) for reviews on this subject see: J. M. Hollander and W. L. Jolly, *Accounts Chem. Res.*, **3**, 193 (1970); D. Betteridge and A. D. Baker, *Anal. Chem.*, **42**, 43A (1970); D. M. Hercules, *ibid.*, **42**, 20A (1970), and references cited therein.

(2) T. D. Thomas, *J. Chem. Phys.*, **52**, 1373 (1970).

(3) With half-line widths of 1.0–1.8 eV, peak separations of about 0.5 eV are currently possible using a deconvolution program or a curve resolver. Line-position measurements are accurate to ±0.1 eV; reproducibility is ±0.03 eV.

(4) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Amer. Chem. Soc.*, **86**, 1360 (1964).

(5) Varian IEE (Induced Electron Emission) spectrometer, with spherical electrostatic analyzer.