of a possible inductive effect caused by the difference in hydrogen mass can hardly be estimated at the present stage, but such an effect is probably of minor importance in this case.[8]

Temperature dependence studies are in progress.

Acknowledgments.—We are indebted to Dr. Sture Forsén of the Royal Institute of Technology for recording, interpreting, and discussing n.m.r. spectra. We wish to thank Prof. Bengt Lindberg and Dr. Olof Theander at the Swedish Forest Products Research Laboratory for permission to use the Perkin-Elmer 141 polarimeter and other facilities. This investigation was supported in part by a Public Health Service Postdoctoral Fellowship (GM-11,563) to R. E. Carter from the National Institutes of Health, Division of General Medical Sciences.

(8) See, for example, H. S. Klein and A. Streitwieser, Jr., *Chem. Ind.* (London), 180 (1961); E. A. Halevi, M. Nussim, and A. Ron, *J. Chem. Soc.*, 866 (1963).

(9) Department of Chemistry, University of Göteborg, Gibraltargatan 5A, Göteborg S, Sweden.

Nobel Institute of Chemistry　　　　　Lars Melander[9]
Stockholm 50, Sweden　　　　　　　　　Robert E. Carter

Photoreduction of 2,2-Diphenyl-1-picrylhydrazyl (DPPH) in Hydrocarbons

Sir:

The chemistry of 2,2-diphenyl-1-picrylhydrazyl (DPPH) has been studied by several authors[1-3] while the stability of the radical has been of special interest in the field of paramagnetic resonance. However, little is known about the photochemical reactivity of this important stable radical.[4] A few papers[5-7] have
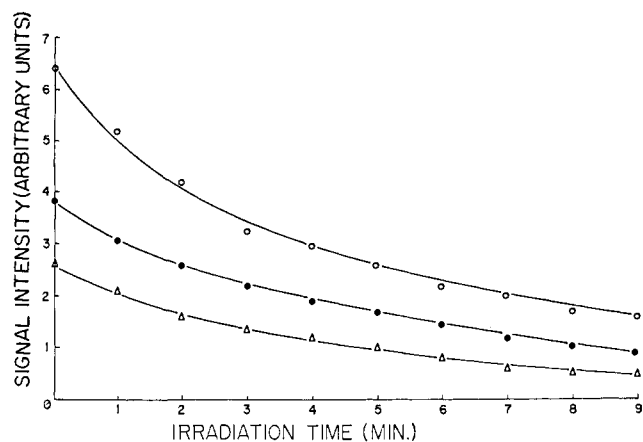

Fig. 1.—Rate of photoreduction of DPPH at various initial concentrations in cumene at 25°, initial concentration of DPPH: $\bigcirc$, 2×10^{-4} mole/l.; $\bullet$, 5×10^{-5} mole/l.; $\triangle$, 2×10^{-5} mole/l.

demonstrated the photo-induced fading of DPPH in aromatic disulfides. However, the disappearance of the DPPH is due to the scavenging reaction of sulfide radicals which are generated in the presence of light.

(1) R. H. Poirier, E. J. Kahler, and F. Benington, *J. Org. Chem.*, **17**, 1437 (1952); R. H. Poirier and F. Benington, *ibid.*, **19**, 1157 (1954).

(2) K. E. Russell, *J. Phys. Chem.*, **58**, 1437 (1954); J. S. Hogg, D. H. Lohman, and K. E. Russell, *Can. J. Chem.*, **39**, 1394, 1588 (1961); P. Venker and H. Herzmann, *Naturwiss.*, **47**, 133 (1960).

(3) S. Goldschmidt and K. Renn, *Ber.*, **55**, 628 (1932).

(4) An investigation concurrent with ours but dealing primarily with the kinetics of the photolysis of DPPH in CCl₄ followed spectrophotometrically has recently been reported: A. Suzuki, M. Takahashi, and K. Shiomi, *Bull. Chem. Soc. Japan*, **36**, 644 (1963).

(5) M. Calvin and J. A. Balltrop, *J. Am. Chem. Soc.* **74**, 6153 (1952).

(6) K. E. Russel and A. V. Tobolsky, *ibid.*, **76**, 395 (1954).

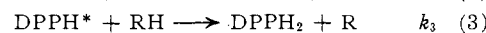(7) V. Schaafsma, A. F. Bickell, and E. C. Kooyman, *Tetrahedron*, **10**, 76 (1960).

We report here the results of a preliminary e.p.r. investigation of the photo-induced abstraction of hydrogen atoms from hydrocarbons by DPPH. The photochemical reaction was carried out at room temperature within the microwave cavity of a Varian e.p.r. spectrometer with 100-kc. field modulation. The light source was a PEK mercury medium-pressure lamp with suitable filters placed at a distance of 100 cm. from the cavity. Solutions to be studied were degassed under vacuum and filled with purified nitrogen at atmospheric pressure. The determination of the approximate amount of light absorbed by DPPH solutions at 3130 Å. was carried out using the photochemical disappearance of benzophenone and the formation of acetone in isopropyl alcohol as an actinometer.[8,9] The benzophenone concentration was adjusted so that the fraction of light absorbed at 3130 Å. matched that absorbed by the DPPH solution.

Although DPPH has absorption maxima at 520 and 330 mμ, we observed that the photoreaction proceeds rapidly enough for e.p.r. measurement only on irradiation in the shorter wave length band. The rates of the photoreduction were followed by recording the relative spin concentration as a function of time at a constant magnetic field, the latter being adjusted to give maximum response. In the dark no diminution in e.p.r. signal intensity was observed; however, during irradiation the e.p.r. signal decreased according to the first-order rate law. A typical curve for the disappearance of DPPH in isopropylbenzene is shown in Fig. 1.

It has been reported that the e.p.r. signal of DPPH in impure isopropylbenzene solution gives a triplet spectrum instead of a quintet.[10] We observed the same triplet spectrum when the isopropylbenzene used was not carefully purified. However, when chromatographically purified isopropylbenzene was used, the ordinary five-line spectrum was obtained. In addition, we also observed a triplet spectrum when DPPH was dissolved in solvents such as hexene and cyclohexene. In the ultraviolet absorption spectrum of these solutions the maximum at 330 mμ was shifted to 345 mμ, suggesting some probable complex formation.

The kinetics of the disappearance of DPPH were also checked by following the reaction colorimetrically; the results agree within about 5%.

The experimental data obtained to date are insufficient to establish the entire reaction mechanism, but seem to fit the sequence

$$\text{DPPH} + h\nu \longrightarrow \text{DPPH*} \qquad I_a \quad (1)$$
$$\text{DPPH*} + \text{RH} \longrightarrow \text{DPPH} + \text{RH} \qquad k_2 \quad (2)$$
$$\text{DPPH*} + \text{RH} \longrightarrow \text{DPPH}_2 + \text{R} \qquad k_3 \quad (3)$$
$$\text{R} + \text{DPPH} \longrightarrow \text{DPPHR} \qquad k_4 \quad (4)$$

In the experiment the hydrocarbon RH is the solvent so that its concentration is practically constant. If reaction 4 is assumed to be rapid, reaction 3 is slow and rate-determining, and fluorescence is negligible, the following kinetic expression is obtained

$$k_2/k_3 = (2/\phi) - 1 \qquad (5)$$

where ϕ is the quantum yield of the disappearance of DPPH. If ϕ is measured the values of k_2/k_3 can be calculated for different solvents. A summary of the experimental results is given in Table I.

We have also briefly studied the photochemical reaction of DPPH in the solid state with infrared spectrometry. The DPPH was mixed with KBr powder and a pellet was formed. The reaction was carried out with the pellet in a Perkin-Elmer 221 infrared spectro-

(8) J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Pecktenwald, and R. B. Martin, *J. Am. Chem. Soc.*, **81**, 1068 (1959).

(9) A. C. Testa, *J. Phys. Chem.*, **67**, 1341 (1963).

(10) H. Ueda, E. Kuri, and S. Shida, *J. Chem. Phys.*, **36**, 1676 (1962)

TABLE I

QUANTUM YIELDS AND RELATIVE RATE CONSTANTS OF DPPH PHOTOREDUCTION IN VARIOUS SOLVENTS

Solvent	k (e.p.r.), min.$^{-1}$	k (col.), min.$^{-1}$	ϕ^a	ϕ^b	k_2/k_3
Benzene	Slow				
Cumene	0.198	0.212	1.3	1.2	0.66
Toluene	.0538	...	0.53	0.48	3.16
Hexane	.0388	0.0411	.38	.35	4.71
Cyclohexane	.0608	0.0648	.57	.54	2.70
Methylcyclohexane	.0823	...	.75	.72	1.77

^{a} Determined using disappearance of Ph_2CO in IPA as an actinometer. ^{b} Determined using formation of acetone in Ph_2CO–IPA photolysis as an actinometer.

photometer with the exciting light (>3100 Å.) at an angle to the pellet. In the absence of light no reaction was observed; however, during irradiation the pellet gradually turned from purple to yellow and the infrared spectrum changed from that of the DPPH to one identical with $DPPH_2$. Further studies of this effect are being conducted and we are now extending this technique to some quantitative studies of photochemical reactions in the solid state.

DEPARTMENT OF CHEMISTRY   J. N. PITTS, JR.
UNIVERSITY OF CALIFORNIA   E. A. SCHUCK
RIVERSIDE, CALIFORNIA   J. K. S. WAN

Circular Dichroism and Rotatory Dispersion Curves for Helices[1]

Sir:

The excited state of a polymeric array can be considered an exciton band of many, closely spaced energy levels. A transition to one of these levels can have a large rotational strength and a small oscillator strength or vice versa, therefore a simple proportionality between the entire absorption band and the circular dichroism curve is not necessarily expected. For a helix the component of the absorption band polarized perpendicular to the helix axis gives rise to a unique circular dichroism curve as shown in Fig. 1. Qualitatively, the shape of the circular dichroism curve arises from many rotational strengths occurring near λ_0, the wave length of maximum absorption of the perpendicular band. The rotational strengths are all positive on one side of λ_0 and negative on the other. They decrease in magnitude as $|\lambda - \lambda_0|$ increases and the sum of all rotational strengths is zero. This leads to canceling of the circular dichroism at λ_0 and nearly equal and opposite curves on either side as seen in Fig. 1. The rotational strengths responsible for this circular dichroism curve were ignored in Moffitt's[2] classical paper. As his original approximation led to only one transition at λ_0 (instead of many near λ_0), the one rotational strength (equivalent to the sum of present rotational strengths) was equal to zero. Moffitt, Fitts, and Kirkwood[3] corrected the mistake, but did not discuss circular dichroism or optical rotatory dispersion near an absorption band. Mason's[4]

(1) Supported in part by research grant GM-10840 from the Institute of General Medical Sciences Public Health Service, by an unrestricted grant from Research Corporation, and by the U. S. Atomic Energy Commission.
(2) W. Moffitt, J. Chem. Phys., 25, 467 (1956).
(3) W. Moffitt, D. D. Fitts, and J. G. Kirkwood, Proc. Natl. Acad. Sci. U. S., 43, 723 (1957).
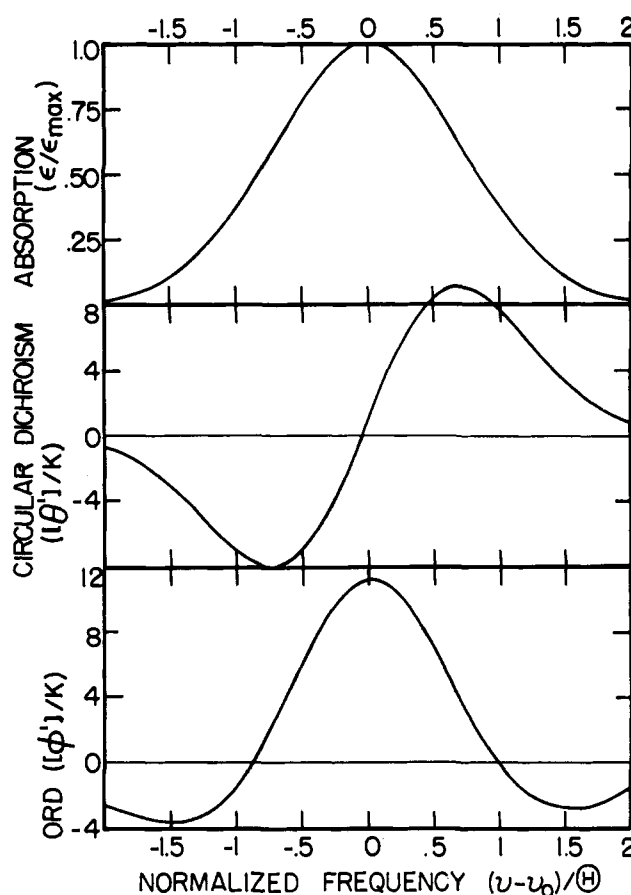(4) S. F. Mason, Quart. Rev. (London), 17, 20 (1963).

Fig. 1.—The absorption, circular dichroism, and optical rotatory dispersion for a perpendicularly polarized band in a helix. The absorption is assumed to be gaussian in frequency (ref. 5) and K is defined in ref. 6.

recent claim that this correction is unimportant is wrong.

The circular dichroism curve seems broader than the absorption curve, because its maximum and minimum occur where the absorption has fallen to about 60% of its maximum value.[5] The sign of the circular dichroism curve is determined by $\sum\limits_{j>i}^{N} (j - i) V_{ij}$ $\sin 2\pi j/P$, where V_{ij} is the potential of interaction of groups i and j and P is the number of groups per turn.[6] The predicted rotatory dispersion (ORD) curve can be obtained from the Kronig–Kramers relation[9] and is also given in Fig. 1.

These curves provide a different interpretation for the recently published circular dichroism data on polynucleotides.[10] For poly A, Brahms finds (ref.

(5) For an absorption curve gaussian in frequency, the maximum and minimum in the circular dichroism curve appear approximately at $\nu - \nu_0 = \pm\Theta/\sqrt{2}$, therefore this corresponds to $\epsilon = \epsilon_{max} \exp[-(\nu - \nu_0)^2/\Theta^2] = \epsilon_{max} \exp(-1/2)$.

(6) The equation for the circular dichroism curve for a single strand helix corresponding to a gaussian absorption curve polarized perpendicular to the helix axis is

$$[\theta'] = K[2(\nu - \nu_0)\nu_0/\Theta^2 + 1] \exp[-(\nu - \nu_0)^2/\Theta^2]$$

$$K = (48\pi^5/2 N_0 z \nu_0 \mu_\perp^2/h^2 c^2 \Theta)\left[\sum\limits_{j>i}^{N} (j - i) V_{ij} \sin 2\pi j/P\right]$$

where z is the pitch of the helix and $\mu_\perp$ is the electric transition moment. It can be derived from an expression for rotational strength for light incident parallel to the helix axis. A very similar expression holds for a double stranded helix.[7]

(7) I. Tinoco, Jr., R. W. Woody, and D. F. Bradley, J. Chem. Phys., 38, 1317 (1963).[8]

(8) See eq. A12 and A14 for the single strand helix and eq. A20 and A21 for the double strand helix.

(9) A. Moscowitz, Advan. Chem. Phys., 4, 67 (1962).

(10) J. Brahms, J. Am. Chem. Soc., 85, 3298 (1963).