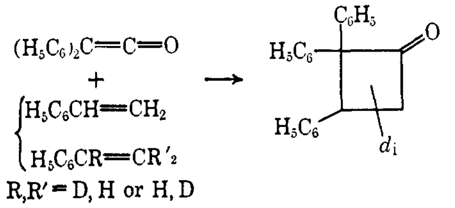
k_H/k_D at 65° per deuterium at the β position of styrene determined through intermolecular competition experiments is 0.91—an inverse effect, as expected; but k_H/k_D for substitution at the α position is 1.23!



The kinetic isotope effects determined in a series of runs are given in Table I.

Table I. Secondary Deuterium Isotope Effects in (2 + 2) Cycloadditions between Diphenylketene and Deuteriostyrenes at 65°

Sample	Run	Molar ratio, styrene/ ketene	k_H/k_D Mass spec	k_H/k_D 100-MHz nmr
$H_5C_6CD{=}CH_2$	1	1.70	1.213	1.254
	2	2.86	1.234	1.221
	3	4.01	1.250	*a*
	4	4.37	1.231	1.208
		Av	1.235	1.227
$H_5C_6CH{=}CHD$[b]	5	1.59	0.920	0.936
	6	2.34	0.913	0.899
	7	2.95	0.904	0.903
	8	4.50	0.896	0.902
		Av	0.908	0.910

[a] Insufficient sample for nmr spectrum. [b] Reaction run with β,β-dideuteriostyrene, and k_H/k_D calculated on a per deuterium basis.

Such a substantial normal isotope effect has become associated with the twisting of an sp^2 carbon out of conjugation with an adjacent p orbital as a necessary prelude to bonding with another atom. Such normal isotope effects have usually been observed or interpreted as intramolecular secondary deuterium isotope effects on a product-determining rather than a rate-determining portion of a reaction profile.[9,10]

Excess diphenylketene and styrene give a practically quantitative yield of adduct; with *cis*-β-deuteriostyrene, the addition is fully stereoselective *cis* on the double bond.[11] Thus the observed k_H/k_D of 1.23 may not be rationalized as arising from an intramolecular competition between ring closure and some other process following the rate-determining formation of a single bond and a difunctional intermediate.

The large isotope effects observed in the addition of diphenylketene with styrene imply a significant progress toward bond making at both α and β positions of styrene in the rate-determining activated complex. At the β carbon, the hybridization change $sp^2 \rightarrow sp^3$ is in progress as a new bond is formed between ketene and olefin. At the α carbon, the transition state has a weaker C–H bond than the ground state, so that $\Sigma_i(\bar{\nu}_i(H) - \bar{\nu}_i(H)^{\ddagger})$ is positive and $k_H/k_D > 1$.[6,7]

The orbital symmetry prohibition against a concerted thermal *cis,cis* addition between an olefin and two parallel p orbitals on the C=C bond of the ketene[12] is thus reflected in an asymmetrical transition state characterized not by different extents of the same process but by different modes of approach toward bond making, manifested in contrary secondary deuterium kinetic isotope effects at the two termini of styrene.

Acknowledgment. This investigation was supported in part by National Science Foundation Grants GP 5226 and GP 9259.

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[9] R. J. Crawford and D. M. Cameron, *J. Amer. Chem. Soc.*, **88**, 2589 (1966).

[10] W. R. Dolbier, Jr., and S. H. Dai, *ibid.*, **90**, 5028 (1968).

[11] J. E. Baldwin and J. A. Kapecki, unpublished.

[12] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968), and unpublished.

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Asymmetric Induction in an Outer-Sphere Redox Reaction

Sir:

The experimental observations which we report here bear on two questions important to the theoretical interpretation of redox reactions of the outer-sphere type.[1] These questions are how close together the reactants must approach in order for the electron to be transferred and whether there is any preferred relative orientation of the reactants. In general, theoretical treatments of this type of electron-transfer reaction assume the reactants to have spherical symmetry.[2]

The reaction which we have chosen for study is a classic example of the outer-sphere reaction (phen = 1,10-phenanthroline)

$$Co(phen)_3^{3+} + Cr(phen)_3^{2+} \longrightarrow Co(phen)_3^{2+} + Cr(phen)_3^{3+} \quad (1)$$

As is usual with Co(III)–Cr(II) reactions, reaction 1 is very much more rapid than substitution on either Co(III) or Cr(III). When a solution 5×10^{-3} *M* in $CrCl_2$ and 1.5×10^{-2} *M* in 1,10-phenanthroline is mixed with a slight excess of a solution 5×10^{-3} *M* in $Co(phen)_3Cl_3$, the main net change which is observed is the reaction of eq 1.

We have resolved the optical isomers of $Co(phen)_3^{3+}$ by the method of Lee, Gorton, Neumann, and Hunt.[3] When *l*-$Co(phen)_3^{3+}$ is used to oxidize $Cr(phen)_3^{2+}$, the product solution is dextrorotatory, and when *d*-$Co(phen)_3^{3+}$ is the oxidizing agent, the product solution is levorotatory, rotations being measured at the sodium D line. Optical rotatory dispersion curves have been obtained for both isomers of $Co(phen)_3^{3+}$ and for the solutions resulting from the oxidation of $Cr(phen)_3^{2+}$ by optically active $Co(phen)_3^{3+}$. Solutions of *d*-$Co(phen)_3^{3+}$ are strongly dextrorotatory in the region 400–450 mμ. The product solution from the oxidation of $Cr(phen)_3^{2+}$ by *d*-$Co(phen)_3^{3+}$ is strongly levorotatory in this same region. That the change in the sign of rotation during the reaction is due to the formation of an optically active Cr(III) complex was substantiated by separation of the species in the product solution on

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[1] H. Taube, *J. Chem. Educ.*, **45**, 452 (1968).

[2] I. Ruff, *Quart. Rev.* (London), **22**, 199 (1968).

[3] C. S. Lee, E. M. Gorton, H. M. Neumann, and H. R. Hunt, Jr., *Inorg. Chem.*, **5**, 1397 (1966).

Dowex 50W-X2 cation-exchange resin. The $Cr(phen)_3^{3+}$ fraction separated cleanly from the unreacted $Co(phen)_3^{3+}$ and was found to account almost quantitatively for the optical activity of the product solution. When d-$Co(phen)_3^{3+}$ was the reactant, l-$Cr(phen)_3^{3+}$ was the major product, and when l-$Co(phen)_3^{3+}$ was the reactant, d-$Cr(phen)_3^{3+}$ was the major product. From the optical activity of the product and the known[3] molar rotations of $Cr(phen)_3^{3+}$ and $Co(phen)_3^{3+}$, we estimate that oxidation of $Cr(phen)_3^{2+}$ by d-$Co(phen)_3^{3+}$ under our experimental conditions results in the formation of about 92% l-$Cr(phen)_3^{3+}$ and about 8% d-$Cr(phen)_3^{3+}$.

Since at the time of mixing $Cr(phen)_3^{2+}$ must be a 1 : 1 mixture of the *d* and *l* isomers the preferential generation of one optical isomer of $Cr(phen)_3^{3+}$ must mean that the redox reaction is substantially slower than the inversion reaction of $Cr(phen)_3^{2+}$, so that the optical isomer of $Cr(phen)_3^{2+}$ which is oxidized more rapidly is constantly replenished. If the redox reaction involving the less reactive isomer were faster than the inversion reaction of $Cr(phen)_3^{2+}$, then the product would be racemic $Cr(phen)_3^{3+}$.

Assuming that at all stages in the reaction the reducing agent is racemic $Cr(phen)_3^{2+}$, we estimate from the product ratios that the activated complex $[l\text{-}Co(phen)_3\text{-}d\text{-}Cr(phen)_3]^{5+}$ is about 1.2 kcal/mole more stable than the activated complex $[l\text{-}Co(phen)_3\text{-}l\text{-}Cr(phen)_3]^{5+}$. Since the energy of the separated reactants does not depend on optical configuration, our observations establish unequivocally that the reactants do not behave as though they had spherical symmetry. There is a configurational restriction on collisions leading to electron transfer. Assuming that the isomers of $Co(phen)_3^{3+}$ and $Cr(phen)_3^{3+}$ have the same sign of rotation for the same chirality, the electron transfer occurs more readily if the configurations of oxidizing and reducing agents are mirror images. A further implication of our results is that the two reactants are in intimate contact in the activated complex.

A much smaller effect of optical activity on reaction rate has been observed by Bruning and Weissman[4] for the electron-transfer reaction between potassium 1-(α-naphthyl)-1-phenylethanide and 1-(α-naphthyl)-1-phenylethane. Asymmetric induction is in principle a much more sensitive technique for probing the effect of optical activity on reaction rates than is the direct measurement of reaction rates as used by Bruning and Weissman. The generation of an optically active product from an inactive reactant is definite evidence for an effect of optical activity on rate, whereas small differences in directly measured rate constants may be due to experimental errors.

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[4] W. Bruning and S. I. Weissman, *J. Am. Chem. Soc.*, **88**, 373 (1966).

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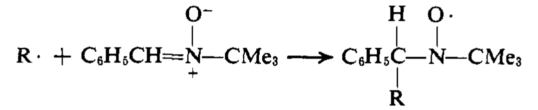
Substituent Effects on the Photochemistry and Nitroxide Radical Formation of Nitro Aromatic Compounds as Studied by Electron Spin Resonance Spin-Trapping Techniques[1]

Sir:

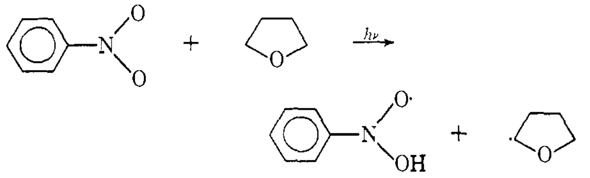
In connection with a general study of substituent effects on the electron spin resonance (esr) spectra of stable free radicals,[2] *meta-* and *para*-substituted nitrobenzenes have been photolyzed in tetrahydrofuran (THF) at room temperature and the esr spectra of the produced radicals obtained. In order to (1) establish the structure of the radicals produced and (2) provide an understanding of the photochemical process and subsequent reactions involved, recently developed spin-trapping techniques[3] have been applied to the study of this problem. This method involves addition of reactive free radicals to phenyl-*t*-butylnitrone (a "spin trap") to produce relatively stable *t*-butyl(α-substituted benzyl) nitroxides ("spinadducts "). The spin adducts



$$R\cdot + C_6H_5CH{=}\overset{O^-}{\underset{+}{N}}{-}CMe_3 \longrightarrow C_6H_5\overset{H}{\underset{R}{C}}{-}\overset{O\cdot}{N}{-}CMe_3$$

are detected by esr and the structure of R· is deduced from a comparison of the nitrogen and β-hydrogen coupling constants (N and β-H hfsc's) of the spin adduct with values obtained from spectra of authentic samples of the nitroxide.[3b,c] By this method methyl, trifluoromethyl, ethyl, *n*-butyl, benzyl, phenyl, acetoxy, benzoyloxy, and *t*-butoxy radicals have been detected.[3]

Ward[4] first published the esr spectrum of the radical produced from the photolysis of nitrobenzene in THF: $A_N = 15.00$, $A^H_{o,p} = 3.1$, $A^H_m = 1.08$, $A^H_{OH} = 0.38$ G. Ward "suspected" that the unique coupling was due to the hydrogen bonded to oxygen, and subsequent workers (including ourselves) have assumed this to be



(1)

correct.[5] However attempts to prepare the same radical by photolysis of nitrobenzenes in the presence of other good hydrogen atom donors either have been futile or have given other radicals.[6] The Ward spectrum can be obtained in THF containing lead dioxide[6b] or saturated with water. It is well known that the

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[1] Research supported by AFOSR(SRC)-OAR USAF Grant No. 1069-66.

[2] (a) E. G. Janzen, O. W. Maender, and J. L. Gerlock, Abstracts of Papers, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 10–15, 1967, S-73; (b) E. G. Janzen, *Accounts Chem. Res.*, in press.

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[6] (a) Unpublished work of J. L. Gerlock; (b) unpublished work of O. W. Maender.