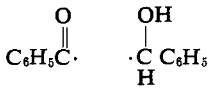
and during optical irradiation, respectively. That the enhancement is quite large can be seen by comparing Figure 1f with Figure 1g which is the spectrum obtained after the sample has been irradiated for 2 min. All three spectra are time avaerages of two scans. Thus benzaldehyde is formed by the photolysis of benzoin, and the aldehyde protons are polarized. Furthermore, the nmr spectrum of benzaldehyde during irradiation (Figure 1b) is very similar to the nmr spectrum of benzoin during irradiation (Figure 1f). In fact, the chemical shift between the aldehyde proton line and the emission line that occurs at higher field is the same in both Figure 1b and f. Furthermore, this chemical shift is identical with the chemical shift between the aldehyde proton line and the lone line which occurs at the highest field in the normal nmr spectrum of benzoin (Figure 1e). We assign this line to the nonaromatic CH proton of benzoin. The structure of benzoin, labeled B, is given below.

The radical-pair mechanism which is consistent with these results is given in eq 2.[10] In this equation, A

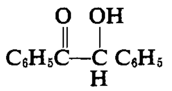
$$\begin{gathered} A \xrightarrow{h\nu} A^* \\ A^* + A \longrightarrow [D] \longrightarrow B \\ [D] \longrightarrow 2A \\ B \xrightarrow{h\nu} B^* \longrightarrow D \end{gathered} \qquad (2)$$

signifies the aldehyde, [D] signifies the radical pair, B signifies benzoin, and the asterisk signifies an excited molecule. [D] and B are shown below.[11] The radical pair is necessary to make the mechanism consistent with the fact that the enhancement of the aldehyde proton nmr line occurs as soon as irradiation is started. Out of necessity, some aspects of this mechanism have been left vague. For example, the benzaldehyde excited state which is involved in the dimerization has not been specified. At this point, we have no evidence to distinguish between the excited singlet and triplet states. Furthermore steps such as D → A* + A and D → B* have not been included since we have no evidence for them. However, they may occur, and we are studying this possibility. Finally, while the point in the mechanism at which the polarization occurs cannot be specified exactly, there are at least two possibilities. The polarization can occur in the radical pair itself or during its formation or dissociation. In the former case, the polarization would result from dynamic nuclear polarization, the Overhauser effect.[2] In the latter case, the polarization results because of the reaction. A number of workers[3,12,13] have obtained evidence for "reaction polarization"; however, its mechanism is still not completely understood.



$C_6H_5\overset{\large O}{\overset{\|}{C}}\cdot \quad \cdot\underset{H}{\overset{OH}{\overset{|}{C}}}C_6H_5$

[D]



$C_6H_5\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{OH}{\overset{|}{C}}}C_6H_5$

B

In conclusion, we have used nmr and the nuclear polarizing effect of unpaired electrons to study the photolysis of benzaldehyde in solution at room temperature. The observed polarization of the aldehyde proton indicates that one of the photolytic processes involves a radical-pair intermediate. The other processes are currently under study.[13a]

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(10) Other processes may be occurring also. For example, the photolysis of benzaldehyde may result in the formation of the phenyl radical. At the present time we are investigating this possibility.

(11) Closs observed nuclear polarization during the photoinduced reduction of benzophenone and concluded that the ketyl of benzophenone was involved in the polarization; see G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **91**, 4550 (1969).

(12) H. R. Ward, R. G. Lawler, H. Y. Loken, and R. A. Cooper, *ibid.*, **91**, 4928 (1969).

(13) L. E. Closs and G. L. Closs, *ibid.*, **91**, 4549 (1969).

(13a) NOTE ADDED IN PROOF. In a personal communication to the authors, Dr. G. L. Closs has indicated that the results of his study of halogen-substituted benzaldehydes corroborate and elucidate further the mechanism proposed in this communication.

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The Simultaneity of Allene Cycloadditions. II.[1] The Dimerization of Allene

Sir:

During the last couple of years there has been much speculation as to the mechanisms of (2 + 2) cycloaddition reactions of ketenes and allenes. This has largely been motivated by the statements of Woodward and Hoffmann[2] to the effect that, unlike other (2 + 2) cycloadditions, those of ketene and allene on theoretical grounds might very well be concerted. Indeed, Huisgen and others have gathered much experimental evidence in support of such a concerted pathway for many (2 + 2) cycloadditions of ketenes.[3]

The high stereoselectivity of a few (2 + 2) cycloadditions of allenic systems pointed toward the possibility that these reactions too were concerted.[4-6] Our recent studies on the secondary deuterium isotope effects of allene cycloadditions,[1] and those of Baldwin,[5] seem, however, to indicate that at least those reactions which we have investigated are nonsynchronous processes; that is, they pass through *two* transition states, the first of which apparently does not discriminate appreciably isotopically, and the second of which shows a significant secondary deuterium isotope effect.[7]

Nevertheless, the very interesting recent work of Moore and coworkers,[6] on the quite stereoselective dimerization of optically active 1,2-cyclononadiene, has been put forward, speculatively, by Hoffmann[9] as a possible example of a *concerted* (2 + 2) cycloaddition of

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(1) Part I: W. R. Dolbier and S. H. Dai, *J. Amer. Chem. Soc.*, **90**, 5028 (1968).

(2) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968), and unpublished results.

(3) R. Huisgen and L. A. Feiler, *Chem. Ber.*, **102**, 3391 (1969), and following papers.

(4) E. F. Kiefer and M. Y. Okamura, *J. Amer. Chem. Soc.*, **90**, 4187 (1968).

(5) J. E. Baldwin, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, ORGN 003; J. E. Baldwin and U. V. Roy, *Chem. Commun.*, 1225 (1969), and personal communication.

(6) W. R. Moore, R. D. Bach, and T. M. Ozretich, *J. Amer. Chem. Soc.*, **91**, 5918 (1969). We thank Dr. Moore for communicating his results to us prior to publication.

(7) In the (2 + 2) cycloaddition of 1,1-dideuterioallene to both acrylonitrile and 1,1-dichloro-2,2-difluoroethylene, significant *intra*molecular secondary deuterium isotope effects were detected, but intermolecular effects were found to be very small, if not negligible.[1,5,8]

(8) S. H. Dai, Masters Thesis, University of Florida, Gainesville, Fla., 1969.

(9) R. Hoffmann, Abstracts, 21st National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, June 1969, p 109.

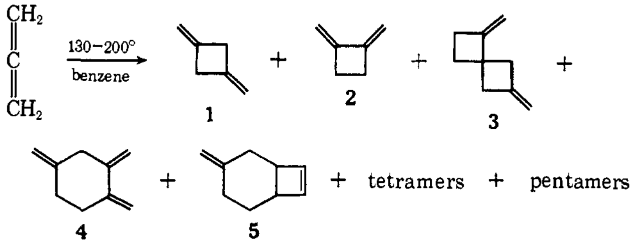
Table I. Intermolecular Isotope Effects. Dimerization of Allene[a,b]

Run	Allene composition, before reaction[c]	Allene composition, recovered[c]	Dimer isotopic composition, observed	Dimer isotopic composition, statistical[c]	k_H/k_D[d]	$(k_H/k_D)^2$[e]
	d_4 49.3 ± 0.1	d_4 50.5 ± 0.1	d_8 24.2 ± 0.4	d_8 24.4 ± 0.1		
1	d_0 50.7 ± 0.1	d_0 49.5 ± 0.1	d_4 49.7 ± 0.2	d_4 49.9 ± 0.4	1.021 ± 0.028	1.020 ± 0.036
			d_0 26.1 ± 0.3	d_0 25.7 ± 0.2		
	d_4 49.9 ± 0.3	d_4 49.3 ± 0.5	d_8 24.5 ± 0.2	d_8 24.8 ± 0.3		
2	d_0 50.1 ± 0.3	d_0 50.7 ± 0.5	d_4 49.9 ± 0.1	d_4 49.9 ± 0.7	1.022 ± 0.018	1.036 ± 0.037
			d_0 25.6 ± 0.1	d_0 25.1 ± 0.3		
	d_4 48.7 ± 0.1	d_4 48.0 ± 0.2	d_8 23.6 ± 0.2	d_8 23.7 ± 0.1		
3	d_0 51.3 ± 0.1	d_0 52.0 ± 0.2	d_4 50.1 ± 0.1	d_4 49.9 ± 0.1	0.997 ± 0.013	1.004 ± 0.024
			d_0 26.3 ± 0.2	d_0 26.4 ± 0.1		
					Av 1.013 ± 0.020	1.020 ± 0.032

[a] The temperature of all reactions was 130°, the time of reaction ranged from 12 to 14 hr, and the per cent conversion ranged from 4.1 to 6.3%. [b] The yields of 1,2-dimethylenecyclobutane were 92–95%. [c] Only d_4 and d_0 allenes were considered and d_8, d_4, and d_0 dimers since the small amount (<6%) of d_3 allene did not complicate the mass spectral analysis. [d] Calculated from the d_4/d_0 ratio of dimers as obtained from low-voltage mass spectra where generally less than 5% fragments were observed. [e] Calculated from the d_8/d_0 ratio.

an allene. We wish, therefore, to report some preliminary results from our laboratory on secondary deuterium isotope effects in the dimerization of allene itself. Initially we had little hope of studying the parent system since work both in static systems[10] and in flow systems[11] had resulted in yields of no better than 5 and 50%, respectively. Much higher yields are necessary since the trimers, tetramers, and higher oligimers observed in these reactions all derive from the initially formed dimer and such destruction would cause the observed k_H/k_D value to be an inaccurate measure of the actual k_H/k_D. We found, however, that by using benzene as a diluting solvent and by working at low temperatures and small fractions of conversion, we were able to increase the yield of 1,2-dimethylenecyclobutane to as high as 95%.

By increasing the temperature, the concentration of allene, or the time of reaction, one could, of course, increase the production of higher oligimers. These oligimers were collected, characterized, and found to be identical with those obtained by Weinstein.[10,12]



With such a high yield possible for the dimer, we were encouraged to investigate the kinetic inter- and intramolecular secondary deuterium isotope effects in the dimerization of allene. In determining the intermolecular isotope effects, approximately equimolar mixtures of tetradeuterioallene and allene were dimerized. The results are summarized in Table I. With an average value of 1.013 ± 0.020 for k_H/k_D, it is clear that there is very little intermolecular discrimination in this reaction, an observation usually taken to mean that the rate-determining step does *not* involve appreciable disturbance at the isotopically labeled site.

Table II. Intramolecular Isotope Effects. Dimerization of Allene[a]

Runs	Allene deuterium content,[b] %	Nmr allyl/vinyl ratio	k_H/k_D
1	100 d_0	1.00 ± 0.03	
2	95.5 d_2 3.86 d_1	1.16 ± 0.02	1.16 ± 0.02
3	95.7 d_2 3.80 d_1	1.13 ± 0.01	1.13 ± 0.01
4	95.5 d_2 3.72 d_1	1.14 ± 0.01	1.14 ± 0.02

[a] Temperature of all runs was 140 ± 2°, the reaction times ranged from 13 to 24 hr, the ratio of benzene/allene from 1.2 to 1.9, and the % of allene reacted from 5 to 8%. [b] The deuterium content of the recovered allene from each run, as measured by low voltage mass spectrometry, was virtually identical with that of the starting allene.

When 1,1-dideuterioallene is allowed to dimerize under similar conditions, with yields between 80 and 85%, an intramolecular kinetic isotope effect of k_H/k_D = 1.14 ± 0.02 is observed as shown in Table II.

While the intramolecular results seem to indicate that isotopic discrimination is occurring at some time during the course of the reaction, the intermolecular competition experiments seem to indicate that it cannot be during the rate-determining step. This being the case, the logical conclusion is that there is *more than one* energy barrier in the mechanistic pathway.[13]

A two-step mechanism can be reconciled with the stereoselectivity which has been observed by Kiefer, Baldwin, and Moore as has been discussed in some detail by Jacobs[14] and by Moore. In these cases, it is apparent that any intermediates that are formed must retain their stereochemical integrity to a considerable extent. A

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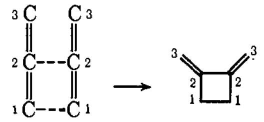
(10) C. B. Lebedev, *J. Russ. Phys. Chem. Soc.*, **45**, 1357 (1913); *Chem. Abstr.*, **9**, 799 (1915); B. Weinstein and A. H. Fenselau, *J. Chem. Soc., C*, 368 (1967).

(11) A. T. Blomquist and J. A. Verdol, *J. Amer. Chem. Soc.*, **78**, 109 (1956); Ya. M. Slobodin and A. P. Khitrov, *J. Gen. Chem. USSR*, **33**, 146 (1963).

(12) B. Weinstein and A. H. Fenselau, *J. Org. Chem.*, **32**, 2278 (1967); **32**, 2988 (1967).

(13) An intriguing alternative explanation has been hypothesized by Dr. W. R. Moore as being consistent with the results. One needs merely to assume (not totally unreasonable) that an isotope effect will be associated with C_3 in the concerted cycloaddition and that $(k_H/k_D)_1$



$(k_H/k_D)_3 \approx 1$, a net cancelling effect. We presently tend to discount this possibility, however, since the large bulk of *experimental* evidence seems to indicate that $(k_H/k_D)_1$ should be <1.00 in a concerted process, while the above hypothesis would *necessitate* that $(k_H/k_D)_1$ be >1.00, an expectation with little available analogy.

(14) T. L. Jacobs, J. R. McClenen, and O. J. Muscio, Jr., *J. Amer. Chem. Soc.*, **91**, 6038 (1969); O. J. Muscio, Jr., and T. L. Jacobs, *Tetrahedron Lett.*, 2867 (1969).

decision as to whether these observations are due to a kinetic factor[15] or whether an actual *structurally rigid* intermediate is involved would be somewhat premature at this time. Suffice it to say that, by all analogy presently available on kinetic secondary deuterium isotope effects, (2 + 2) cycloadditions of allene, *including dimerizations*, appear to proceed *via* nonsynchronous pathways.

Acknowledgments. We are pleased to acknowledge partial support of this work by the National Science Foundation (Grant No. GP 8320).

(15) Nonbonded interactions in possible diradical intermediates might very well slow down bond rotations drastically within the intermediates and thus allow ring closures to be relatively quite rapid.

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Excited States in the Ultraviolet Photochemistry of Cobalt(III) Complexes. Evidence from Chemical Scavenger Studies of $Co(NH_3)_5O_2CCH_3{}^{2+}$ at 254 nm[1]

Sir:

Most of the ultraviolet photochemistry of cobalt(III) complexes arises from the irradiation of absorption bands possessing charge-transfer (CT) character and results in oxidation–reduction processes and, to a lesser extent, ligand-exchange reactions.[2–6] Although radical transients have been observed under flash photolysis conditions,[7,8] the precursors of these radicals appear to be so short-lived as to preclude direct observation or to affect the formation kinetics of the observable transients.[8] Thus, it has been difficult to provide evidence which can distinguish between the radical pair[2] and excited-state[3,4] mechanisms that have been proposed to account for the photochemistry of cobalt(III) complexes. One potentially powerful technique which has not been exploited to any great extent in the photochemistry of complex ions is the use of nonabsorbing reactive chemical scavengers to distinguish between the mechanistic possibilities. We wish to describe the investigation of short-lived intermediates using chemical scavenging techniques.

Although it is possible to alter the distribution and yields of oxidized products,[2,3,7–10] it has proven very difficult to find nonabsorbing scavengers which can alter the primary quantum yield of Co^{2+} formation, $\phi_{Co^{2+}}$. We have found[3] that $\phi_{Co^{2+}}$ is often a function of $[H^+]$, implying that excited-state intermediates have acidities different than those of the ground-state complexes. Our observation[11] that the addition of $[CH_3OH] \geq 5\ M$ to $Co(NH_3)_5Cl^{2+}$ increases $\phi_{Co^{2+}}$ nearly threefold has led us to apply the use of such nonabsorbing scavengers to systems where the photochemistry is relatively straightforward.

Table I. Quantum Yields of Products[a]

Product	ϕ	Product	ϕ
Co^{2+}	0.190 ± 0.007^b	C_2H_6	0.07 ± 0.02^c
CO_2	0.15 ± 0.02^c	H_2	Trace
CH_4	0.008 ± 0.002^c	N_2	Not detectable

[a] $[Co(NH_3)_5O_2CCH_3{}^{2+}] = 5.0 \times 10^{-3}\ M$; $[HClO_4] = 0.1\ M$; 25°. [b] $I_a \simeq 5.5 \times 10^{-4}$ einstein $l.^{-1}\ min^{-1}$. Error limits are the average deviations of four determinations. [c] $I_a \simeq 6.5 \times 10^{-3}$ einstein $l.^{-1}\ min^{-1}$. Error limits are the average deviations of eight determinations. The ratio $\phi_{CH_4}/\phi_{C_2H_6}$ decreases with increased light intensity but the sum $(\phi_{CH_4} + 2\phi_{C_2H_6})$ does not vary significantly with I_a.

$[Co(NH_3)_5O_2CCH_3](ClO_4)_2$ was prepared as described in the literature[12] and was recrystallized until the absorption spectrum agreed with that in the literature. Solutions were prepared with distilled water and reagent grade chemicals. The photochemical techniques employed have already been described.[3,9,10] Product gases were identified mass spectrometrically and yields were determined by quantitative vpc (molecular sieve column and thermal conductivity detection).

Table I summarizes our determinations of the quantum yields of product formation in the absence of scavengers.[13] These yields are not noticeably dependent on $[H^+]$. Note that $\phi_{Co^{2+}} \simeq \phi_{CO_2} \simeq (\phi_{CH_4} + 2\phi_{C_2H_6})$, indicating the accountability of all electron equivalents. $\phi_{Co^{2+}}$ is unaffected by $[CH_3OH] \leq 2.5\ M$ but is increased in the presence of 2-propanol, reaching a limiting value of ~0.4 at high concentrations (Figure 1). ϕ_{CO_2} is not significantly affected by the presence of either alcohol and, although ϕ_{CH_4} is increased and $\phi_{C_2H_6}$ is decreased as [alcohol] is raised, $\phi_{CH_4} + 2\phi_{C_2H_6}$ remains relatively unchanged (Figure 2). Spectral and ion-exchange analyses of irradiated solutions have shown no evidence for photoaquation products.

The stoichiometry demonstrates that the only photoredox process occurring involves the acetate ligand and the cobalt center.

$$Co(NH_3)_5O_2CCH_3{}^{2+} \xrightarrow[h\nu]{H^+} Co^{2+} + 5NH_4{}^+ + \underset{\llcorner\!\rightarrow \text{ gaseous products}}{CH_3CO_2\cdot}$$

Furthermore, it is clear that the precursor excited states (or, alternatively, radical pairs) leading to the formation of CO_2, CH_4, and C_2H_6 are not scavengeable by either alcohol. It must be concluded, therefore, that absorption of 2537-Å radiation by $Co(NH_3)_5O_2CCH_3{}^{2+}$ leads to two chemically distinguishable intermediates: X*, which is not scavengeable and leads to the gaseous products of the reaction, and Y*, which normally re-

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(1) This work was supported by the National Science Foundation under Grants GP 7048 and GP 11213.

(2) A. W. Adamson, *Discuss. Faraday Soc.*, **29**, 163 (1960).

(3) J. F. Endicott and M. Z. Hoffman, *J. Amer. Chem. Soc.*, **87**, 3348 (1965).

(4) V. Balzani, L. Moggi, F. Scandola, and V. Carassiti, *Inorg. Chim. Acta Rev.*, **1**, 7 (1967).

(5) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968).

(6) J. F. Endicott and M. Z. Hoffman, *J. Amer. Chem. Soc.*, **90**, 4740 (1968).

(7) S. A. Penkett and A. W. Adamson, *ibid.*, **87**, 2514 (1965).

(8) G. Caspari, J. F. Endicott, and M. Z. Hoffman, unpublished observations.

(9) R. G. Hughes, J. F. Endicott, and M. Z. Hoffman, *Chem. Commun.*, 195 (1969).

(10) J. F. Endicott, M. Z. Hoffman, and L. S. Beres, *J. Phys. Chem.*, **74**, 1021 (1970).

(11) G. Caspari, R. G. Hughes, J. F. Endicott, and M. Z. Hoffman, manuscript in preparation.

(12) D. K. Sebera and H. Taube, *J. Amer. Chem. Soc.*, **83**, 1785 (1961); L. M. Jackman, R. M. Scott, and R. H. Portman, *Chem. Commun.*, 1338 (1968).

(13) In addition to the equality of $\phi_{Co_2{}^+}$ and ϕ_{CO_2} reported here, the fact that no N_2 generation in the photolysis of $Co(NH_3)_5O_2CCH_3{}^{2+}$ at 254 nm is observed eliminates any photoredox process leading to N_2 (from NH_2) and CH_3COOH as a mechanistic possibility and negates the recent proposal of such a step: A. W. Adamson, A. Vogler, and I. Lantzke, *J. Phys. Chem.*, **73**, 4183 (1969).