transitions, to give finally a $\Delta M_{\rm S} = -1/_2 \rightarrow 1/_2$ transition at 100 K. EPR spectra of frozen green-brown solutions obtained by dissolving the green complex in solvents such as DMF, Me₂SO, or CH₃CN gives a typical mixed-valence 16-line pattern. Magnetochemistry studies show that $\mu_{\rm eff}/Mn$ for the green powder decreases from 2.1 $\mu_{\rm B}$ at 300 K to 0.71 $\mu_{\rm B}$ at 1.9 K. An intramolecular antiferromagnetic interaction with J = -54 cm⁻¹ was found on fitting the experimental data to the equations for an exchange interacting ($S_1 = 5/_2$, $S_2 = 2$) dimer.

Variable-temperature susceptibility results (from 5.9 μ_B at 300 K to 1.86 μ_B at 1.7 K) for a solid sample of the Mn^{II}(saldien) complex indicate a dimeric structure, i.e., [Mn^{II}(saldien)]₂, which is probably similar to that reported⁸ for $[Cu^{II}(saldien)]_2$. Compared to the IR spectrum of Mn^{II}[5-NO₂(saldien)], the CsBr pellet IR spectrum of the green O₂ oxidation product exhibits two peaks at 657 and 793 cm⁻¹ which may be respectively assigned to the Mn-O and the O-O stretching vibrations of a coordinated peroxide group. When the green O_2 oxidation product is heated (180 °C) under vacuum, the color of the powder turns back from green to orange which is the color of Mn^{II}[5-NO₂(saldien)]. Furthermore, the EPR characteristics (solid state and frozen solution) of the orange solid and Mn^{II}[5-NO₂(saldien)] are identical. Efforts are continuing to grow good crystals of the green compound. Taking into account the fact that the O2 oxidation of Mn^{II} complexes with ligands such as saldien gives Mn^{III} as the most oxidized form of the manganese,⁹ we suggest that the green compound consists of two $Mn^{II}Mn^{II}$ (saldien)₂ units bridged by an $O_2^{2^-}$ ion.¹⁰

The frozen-solution EPR spectra of our mixed-valence complexes were simulated in the same manner¹¹ as employed by Cooper et al.⁷ The lower trace (B) in Figure 1 shows the best simulated spectrum obtained for a pair of inequivalent manganese ions; i.e., the Mn^{II}Mn^{III} complex has a localized structure. Small anisotropies in the manganese A and g tensors were incorporated to get the best simulation. The final parameters for the ground-state Kramers doublet of the pair are $g_x = g_y = 2.006$ and $g_z = 2.00; A_{1x} = A_{1y} = 170 \text{ G and } A_{1z} = 156 \text{ G}; A_{2x} = A_{2y} = A_{2z}$ = 83 G. We can recast these hyperfine values into the single-ion values. If the complex is incorrectly assumed to be a Mn^{III}Mn^{IV} complex, we find $A_x = A_y = 85$ G and $A_z = 78$ G for Mn^{III} whereas $A_x = A_y = A_z = 83$ G for Mn^{IV}. If the complex is correctly assumed to be a Mn^{II}Mn^{III} complex $A_x = A_y = 73$ G and $A_z = 67$ G for Mn^{II} whereas $A_x = A_y = A_z = 62$ G for Mn^{III}. The hyperfine interaction calculated for the Mn^{IV} ion (83 G) in the Mn^{III}Mn^{IV} formulation does not agree with the 97 G hyperfine interaction we have determined¹² for a frozen solution of $(Mn^{IV}[5-NO_2(saldien)])(ClO_4)_2$, a mononuclear compound that was prepared electrochemically. For a frozen solution of Mn^{II}-[5-NO₂(saldien)], we find a dimer-type EPR signal with an 11-line S = 0 to S = 1 manganese hyperfine pattern with a splitting of A = 38 G. A value that is twice this dimer interaction (i.e., 76 G) is in better agreement with the 73 G interaction found for the Mn^{II} ion in the Mn^{II}Mn^{III} formulation.

The above analysis suggests that caution has to be exercised in deciding which oxidation states of manganese are present in

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a mixed-valence complex if only the magnitudes of manganese hyperfine interactions are known from EPR simulations. It is quite possible that the hyperfine interaction can vary considerably for a given oxidation state of manganese depending on the coordination number and geometry of the manganese ion.

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Characterization of Transient Intermediates on Laser Flash Excitation of Cyclohexenones in the Presence of Amines¹

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Recently, we reported that upon laser flash photolysis of a series of 2-cyclohexenones, transient absorption could be observed in the ultraviolet region (260-320 nm) whose lifetime correlates with the ability of the enone to twist about the C_2-C_3 double bond.² This structural feature also determines the rate of energy transfer to triplet quenchers such as naphthalene (NA), 1,3-cyclohexadiene (CHD), and piperylene.³ Olefins such as 1,1-dimethoxyethylene (DME) and cyclohexene and amines such as 1,4-diazabicyclo-[2.2.2]octane (DABCO) and triethylamine quench certain photoreactions of these enones but have no effect on the observed transient.² We therefore concluded that for conformationally flexible enones, this transient does not lead to photoproducts.⁴ A "phantom" triplet state, which has not yet been directly detected, was proposed to be responsible for reaction with amines and olefins, as well as triplet energy transfer to NA and CHD.² For conformationally rigid enones, the distinction between the spectroscopically observable species and the chemically reactive triplet state becomes blurred.

We now report that flash photolysis of degassed samples of enones 1-5 in acetonitrile in the presence of tertiary amines using a 353-nm pulse from a mode-locked Nd:YAG laser yielded new long-lived transients absorbing from 260 to 500 nm. Figure 1 shows spectra generated from enones 1, 2, and 4 in the presence of DABCO and N,N-dimethylaniline (DMA).

Flash excitation of DABCO alone in acetonitrile with a 265-nm pulse produces a broad absorption which decays with a lifetime of 22 ns and narrow absorption which decays with $\tau = 4-7 \ \mu s$,

(4) Similar conclusions have been reached by Pienta based on complementary studies. See: Pienta, N. J. J. Am. Chem. Soc. 1984, 106, 2704.

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(b) Coleman, W. M.; Taylor, L. T. Inorg. Chim. Acta 1978, 30, L291–L293.
(10) Peroxide-bridged binuclear manganese complexes have been suggested

⁽¹⁰⁾ Peroxide-bridged binuclear manganese complexes have been suggested by Coleman and Taylor for the oxygenation products of the related Mn^{II}-(XSalDPT) compounds.⁹⁵

^{(11) (}a) The frozen-glass, X-band, EPR spectra were simulated employing the following spin Hamiltonian: $\hat{H} = g_{\parallel}\beta H_x \hat{S}_x + g\beta(H_x \hat{S}_x + H_y \hat{S}_y) + IAS$ The EPR signal is attributable to the ground-state Kramers doublet resulting from an antiferromagnetic exchange interaction between two Mn ions. In the simulation a Gaussian line shape was assumed with the line width of a particular transition determined by the nuclear spin quantum number and the degree of strain in g and A tensors. A computer program based on the following sources was employed: (a) Nilges, M. J. Ph.D. Thesis, University of Illinois, Urbana, IL 1979. (b) Belford, R. L.; Nilges, M. J. "Computer Simulation of Powder Spectra", EPR symposium, 21st Rocky Mountain Conference, Denver, CO, 1979. (c) Maurice, A. M. Ph.D. Thesis, University of Illinois, Urbana, IL, 1980.

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⁽³⁾ For rigid enones such as 4, quenching of the transient absorption at 280 nm by piperylene can be observed directly. However, for flexible enones (e.g., 1 and 3) quenching of this transient by piperylene is inefficient and nonlinear, while no quenching by CHD is observed. Quenching by NA cannot be directly measured at 280 nm due to NA ground-state absorption, but absorption of ${}^{3}NA^{*}$ at 413 nm is easily monitored.^{2a}



both centered at \sim 460 nm. In the presence of electron acceptors such as N_2O or methylviologen, the broad absorption disappeared; in the latter case, the absorption spectrum of the methylviologen radical cation $(\lambda_{max} 603 \text{ nm})^5$ was observed. We therefore conclude that the broad absorption is due to solvated electrons and that the long-lived absorption is due to solvated DABCO radical cations (6). The latter are reported to absorb strongly around 465 nm with ϵ_{max} 2100 $M^{-1}\ cm^{-1\,6a}$ and have an absorption spectrum in rigid glasses at 77 K^{6b,c} very similar to that which we observe in acetonitrile in the presence of N_2O .

The transient spectra in Figure 1 generated on excitation of the enones in the presence of DABCO are remarkably similar to that assigned to $DABCO^+$ (6). We therefore conclude that under these conditions electron transfer occurs to give solvated enone radical anions and 6. This is supported by the observation that the lifetimes of the long-wavelength transients are all essentially equal (Table I). This is a rare case of direct observation of amine radical cations generated from ketone excited states in solution. Roth⁷ has obtained CIDNP evidence for the intermediacy of radical ions in photoreactions of benzophenone derivatives and amines, while Peters8 observed the UV absorption of radical anions of aromatic ketones formed in the presence of amines using picosecond laser spectroscopy.9 Scaiano10 has observed absorption at 480-590 nm on laser flash excitation of acetophenone in the presence of cyclic 1,5-diamines, attributed to the corresponding diamine radical cations.

For enones 1, 3, and 4 at concentrations sufficient to give an optical density of 0.7-1.0 at 353 nm, plots of the rate of formation of 6 (i.e., $1/\tau_{growth}$) were linear with [DABCO], providing rates of quenching (k_a) and extrapolated lifetimes (τ_0) of the enone triplet precursors (Table I). These lifetimes are comparable with those obtained from analogous experiments² involving rates of transfer of triplet excitation from enones to NA in isopropyl alcohol (Table I). The rise time of the enone 2-DABCO transient was reduced in the presence of DME, corresponding to a quenching rate constant of $1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} (\pm 50\%)$, in rough agreement with the previously determined rate constant for interception of the reactive "phantom" triplet of 1 by DME.^{2,11} We therefore conclude that electron transfer occurs from DABCO to the same enone triplet state that is quenched by NA and olefins and that undergoes the lumiketone photorearrangement.^{2,11,12}

With other tertiary amines, specifically triethylamine and N,N-dimethylaniline (DMA), long-lived transients are also seen

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Figure 1. Absorption spectra of transient species generated upon laser flash excitation at 353 nm of enones 1 (a), 2 (b), and 4 (c) in the presence of 0.02 M DABCO (•) and 0.01 M DMA (+). Optical densities of the transients produced from 1 and 2 in the presence of DABCO were measured 180 ns after the flash, while, in the case of 4, measurements were made 150 and 600 ns after the laser pulse using DABCO and DMA, respectively.

Table I. Kinetic Properties of Transient Enone-DABCO Species^a

enone	$\tau_{450}, \mu s$	τ_0 , ^b ns	$k_{\rm a},^{b} {\rm M}^{-1} {\rm s}^{-1}$	τ_0 , ns ^c	
4	1.4-1.9	323	1.2×10^{9}	145 ^d	
1	1.0-1.5	19	2.7×10^{8}	28 ^d	
3	1.0-1.5	16.9	3.7×10^{8}	24 ^e	

^aNumbers are averages of several independent determinations. Estimated experimental uncertainty is 10%. ^b Determined from intercept of plot of $1/\tau_{growth}$ vs. [amine] in acetonitrile. ^cDetermined from intercept of plot of rise time of triplet naphthalene absorption at 413 nm vs. [NA]. ^dSolvent was isopropyl alcohol. ^eSolvent was acetonitrile.

at long wavelengths. We believe that these are not amine radical cations, which ought to be very short-lived because of rapid proton transfer to the enone radical anions, a process that is inhibited structurally in the case of DABCO.¹³ It is likely that the DMA-based transient absorption in Figure 1c is the radical $PhN(CH_3)CH_2$, and not DMA^+ , which has a reported absorption maximum at 460 nm.^{6b,14} Our spectrum for this radical agrees with that reported by Scaiano.15

The dependence of k_a for DABCO on enone structure is shown in Table I. The rate of electron donation from DABCO will depend on the excitation energy of the enone triplet acceptor.¹⁶

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The observation that k_a for enone 4 is greater than that for the monocyclic enones (Table I) is consistent with the earlier proposal¹ that the energy of the reactive π,π^* triplet of these enones decreases as the ability of the triplet to relax by twisting about the C_2 - C_3 bond increases. Furthermore, the low-energy (E_T ca. 50 kcal/mol) long-lived (ca. 10 µs) triplet state of steroidal dienone 7 is not quenched by DABCO, since electron transfer in this case would be highly endothermic.18

We conclude from this study that amines react with relaxed enone π,π^* triplet states by the transfer of an electron and formation of solvated enone radical anions and amine radical cations. In the case of DABCO, the exclusive fate of the radical ion pair appears to be decay to the ground state since no enone-DABCO adducts have as yet been detected, although enone-amine adducts and reduced enone are formed when other tertiary amines are utilized.19,20

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Registry No. 1, 1073-13-8; 2, 6606-34-4; 3, 930-68-7; 4, 58-22-0; 5, 826-56-2; DABCO, 280-57-9; DMA, 121-69-7.

Spectroscopic Determination of σ_{I} and σ_{R} Substituent Constants for the Deuterium Atom

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104. 5501.

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Deuterium-induced differences $\Delta \delta$ in the chemical shifts of carbon atoms of isotopomeric molecules have been investigated by ¹³C NMR spectroscopy for a number of reasons.^{1,2} As a consequence of the Born-Oppenheimer approximation their origin should always be attributed to the difference in vibrational motion of the two isotopes. Yet, the interpretation of the observed isotope-induced shifts is often given in terms of electronic substituent effects. Thus, for example, shifts to lower field of carbon atoms in ortho and para position in side-chain deuterated alkyl derivatives of benzenes³ as well as the dependence of the shifts of both ortho positions of several trideuteriomethylated aromatic systems on π -bond order⁴ have been taken as a manifestation of isotopic perturbation of hyperconjugation. In extension of our earlier work⁵ we have recently discussed isotope-induced π -polarization to account for the experimental results in a series of deuterated derivatives of biphenyl.6

The behavior of the carbon atoms in the unsaturated side chain of the styrene derivatives 1a, 2a, and 3a (X = D), which constitutes

Table I. Long-Range Deuterium Isotope Effects $\Delta \delta$ on ¹³C Chemical Shifts^{*a*} and Substituent Susceptibilities $\rho_{I,R}$ from DSP Analy sis^b

compd		C-5	C-6	C-7	C-8	С-9	ref
s •	${\Delta\delta\over ho_{{ m I}}{}^{i}} ho_{{ m R}}{}^{i}$	8 2.39 0.36	12 4.97 8.89				10
	$\Delta \delta ho_{\mathbf{I}^{i}} ho_{\mathbf{R}^{i}}$	-8 -1.83 0.15	9 4.03 6.97				10
2 >5 ×5 ×	$\Delta \delta ho_{\mathbf{r}_{i}^{i}} ho_{\mathbf{R}}^{i}$	-9 -1.99 -0.36	0 1.91 0.99				10
x	${}^{\Delta\delta}_{{}^{ ho}{ m I}^{i}_{ ho}{ m R}^{i}}$	-6 -5.3 1.23	0 -0.73 0.21	0 0.26 0.17	0 1.15 0.12		16
x	${\Delta\delta\over {\rho_{\rm I}}^i}$	-10 -3.17 -1.14	$\begin{array}{c} 0 \\ 0.41 \\ 1.11 \end{array}$	0 0.49 0.26	4 2.00 2.09		17
x-()-(; , , , , , , , , , , , , , , , , , , ,	${\Delta\delta\over ho_{\rm I}{}^i}_{ ho_{\rm R}{}^i}$	-5 -2.31 0.52	-4 -1.63 -1.83			0 1.35 1.28	18
•	${\Delta\delta\over ho_{\mathbf{I}}^{i}}_{ ho_{\mathbf{R}}^{i}}$	-8 -2.9 -1.8	15 5.1 6.1				19

^a Data given in ppb, spectra recorded at 100.6 MHz on a Bruker WH-400 spectrometer in acetone- d_{6} solutions. All solutions contained unequal amounts of deuterated and parent compounds, errors amount to 0.75 ppb. The sign of the isotope effects follows the convention given by Hansen² and is, unfortunately, opposite to the convention used for substituent effects ($SCS^i =$ $\delta_{\mathbf{R}\mathbf{X}}^{i} - \delta_{\mathbf{R}\mathbf{H}}^{i}$ and $\Delta \delta = \delta_{\mathbf{R}\mathbf{H}}^{i} - \delta_{\mathbf{R}\mathbf{D}}^{i}$.

a definitive experimental test of our proposal, is reported here along with an attempt to correlate a number of long-range deuterium isotope effects with data from studies of common substituent effects.

The para-substituent-induced chemical shift (SCS) of the carbon atoms of the vinyl sidechain in 1-3 has been analyzed by the DSP method⁷⁻⁹ by Reynolds and co-workers.¹⁰ The effect of substituents X on the chemical shifts of the vinyl carbon atoms is given by eq 1. The parameters ρ_{I}^{i} and ρ_{R}^{i} measure the sus-

$$SCS^{i} = \rho_{I}^{i} \sigma_{IX} + \rho_{R}^{i} \sigma_{RX}$$
(1)

ceptibility of the *i*th carbon atom on the polar $(\sigma_{I,X})$ and mesomeric $(\sigma_{R,X})$ nature of the substituent X. ρ_{I}^{i} and ρ_{R}^{i} values obtained from statistical analysis are included in Table I for compounds 1-7. All C-6 atoms of 1-3 show a pronounced susceptibility to the mesomeric influence of substituents X. As the conjugation between the phenyl ring and the vinyl group is diminished by steric

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