dence was found for the involvement of an intermediate, presumably derived from manganese(V), which could further be oxidized by permanganate.[2] This second oxidation step appeared to be of importance in determining which products are formed. We now wish to present direct spectrometric evidence for such an intermediate.

When a large excess of crotonic acid was used at pH 7 the absorbance at 525 mμ decreased in a normal first-order fashion. However, at 420 mμ, the absorbance increased at a corresponding rate. The kinetic behavior was a function of pH. Using 0.2 M sodium hydroxide, the change in absorbance with time at 525 mμ was unchanged. The absorbance at 420 mμ first increased and then decreased, whereas the absorbance at 584 mμ first decreased and then increased.

The spectral changes were monitored at 28 wavelengths and all of the data were treated simultaneously by the method of least squares.[3] The data were consistent with the following scheme

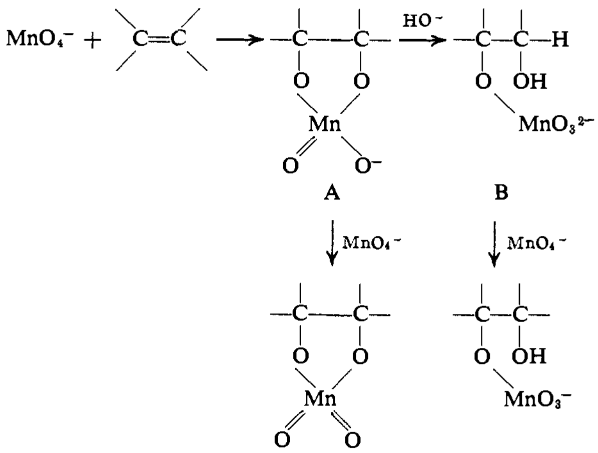
$$CH_3CH{=}CHCO_2^- + MnO_4^- \xrightarrow{k_1} A$$

$$A + HO^- \xrightarrow{k_2} B$$

where $k_1 = 110\ M^{-1}\ \text{sec}^{-1}$ and $k_2 = 10\ M^{-1}\ \text{sec}^{-1}$ (0°). The spectra were obtained *via* this analysis and are shown in Figure 1. The species B reacts further at a slow rate giving manganese dioxide. The spectra of both A and B are markedly different than either permanganate or manganate.

When the ratio of crotonic acid to permanganate was reduced, the spectrum indicated that manganate(VI) began to be formed.[4] A detailed kinetic analysis of the data indicated that both A and B were oxidized by permanganate giving manganese(VI) species.[5] The rate of formation of A was unchanged. Since A and B are converted to manganese(VI) by permanganate, they must be derivatives of manganese(V).

Scheme I



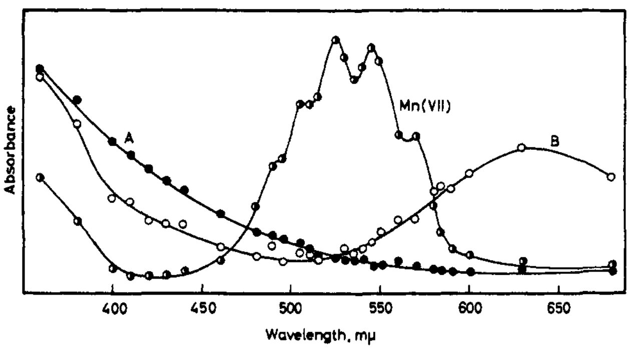


Figure 1. Absorption spectra of permanganate and of the two manganese(V) species, A and B, as determined from an analysis of kinetic data. The absorbance values for B have been multiplied by a factor of two.

These data are in good accord with the scheme (Scheme I) which we proposed previously.[2] The first-formed species, A, is assigned the cyclic structure in accord with the stereochemistry of the diol formation,[6] the observation of oxygen-18 transfer from permanganate,[7] and the present observation that it is converted to another manganese(V) species by base.

The unique observation is the relatively high stability of A in neutral solution. Manganate(V) is stable toward disproportionation only in concentrated potassium hydroxide solutions.[8] Even manganate(VI) is unstable below about pH 10. The high stability of A is probably a result of its being a diester and, thus, being completely ionized even in neutral solution. The base concentrations at which manganate(VI) and manganate(V) are stable are those which would be expected to give essentially complete conversion to the respective anions. Disproportionation may well involve initial anhydride formation which would be facilitated by protonation.

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[3] C. Deutsch, "Computer Programs for Chemistry," Vol. 4, D. F. DeTar, Ed., Academic Press, New York, N. Y., 1972, p 243.

[4] Manganate(VI) has absorption maxima at 439 and 606 mμ. When a 2:1 ratio of permanganate to crotonic acid was used, the spectrum of the reaction solution was the same as that for manganate(VI).

[5] The scheme shown below was employed with a Runge-Kutta numerical integration routine to generate simulated kinetic data. It was possible to adjust the rate constants for oxidation of A and B to give a good fit for a number of crotonate:permanganate ratios ranging from 1000:1 to 1:1. At the high ratio, no manganate(VI) was formed and at the low ratio, manganate(VI) was the only manganese species formed.

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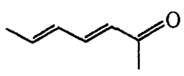
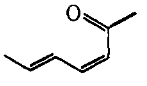
Triplet Sensitized Photoisomerization of 3,5-Heptadienone

Sir:

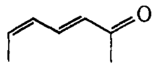
Irradiation of any of the three known isomers of 3,5-heptadienone (tt, ct, and tc) cleanly and rapidly pro-



tt



ct



tc

Table I. Quantum Yields for 3,5-Heptadienone Photoisomerization[a-c]

Conditions	$\phi_{tt\to ct}$	$\phi_{tt\to tc}$	$\phi_{tc\to tt}$	$\phi_{tc\to ct}$	$\phi_{ct\to tt}$	$\phi_{ct\to ct}$	$\Sigma\phi$[d]
Sens (benzophenone)	0.064	0.152	0.240	0.070	0.120	0.029	
Sens (Michler's ketone)	0.066	0.148	0.241	0.071	0.122	0.030	
Sens (av)	0.06	0.15	0.24	0.07	0.12	0.03	0.67
Unsens (λ 254 nm)	0.29	0.15	0.18	0.26	0.36	0.13	1.37
Unsens (λ 313 nm)	0.25	0.16	0.29	0.18	0.24	0.14	1.26

[a] In degassed benzene at 18 ± 2°. [b] Values are the average of results from separate tubes with two vpc analyses per tube and are not corrected for back reaction. Per cent conversion varied between 4 and 6%. [c] Uncertainties are estimated as ±0.01–0.02. [d] Sum of the six quantum yields.

duces the same photostationary mixture.[1-3] Quantum yield studies revealed the occurrence of two-bond one-photon isomerization but ruled out the possibility that isomerization occurred exclusively *via* an excited intermediate common to all three isomers.[1,2] Triplet sensitized isomerization also proceeded smoothly. Sensitizers having triplet energies in excess of 58 kcal/mol produced the same photostationary mixture of isomers.[2] Observation of quantum yield wavelength dependence and the failure of the unsensitized quantum yields to account for the photostationary state composition in the presence of "high-energy" triplet sensitizers led to the suggestion that the unsensitized isomerizations proceeded *via* singlet excited states.[2] We now present data which require this conclusion and demonstrate that, in contrast to isomeric 1,3-dienes,[4] the isomeric 3,5-heptadienones do not give a common triplet upon acceptance of triplet energy.

Irradiation of 3,5-heptadienone isomers in degassed benzene with benzophenone or Michler's ketone as sensitizer under conditions in which the sensitizer absorbed >99.9% of the light cleanly produced the same photostationary mixture previously reported.[2] No side products such as benzophenone photoreduction products could be detected by gas chromatography. Quantum yields were determined by irradiation of pure heptadienone isomers plus sensitizer in degassed benzene solution under conditions in which the sensitizer absorbed >99.9% of the light, and quenching of sensitizer triplet was >99.9% efficient.[5,6] Quantum yield data are presented in Table I. It can be seen that both sensitizers, benzophenone with a lowest triplet of $n\pi^*$ configuration[8] and ϵ_T = 69 kcal/mol[9] and Michler's ketone with a lowest $\pi\pi^*$ triplet[8] at 61 kcal/mol,[9] gave identical results. This is only consistent with a mechanism which involves simple irreversible transfer of triplet energy from sensitizer to all the dienone isomers at equal rates. Assuming an equal rate of energy transfer to all isomers, we have used the quantum yields to calculate a photostationary composition[2] which agrees with that determined experimentally (Table II). Changes of 0.03 unit in any one of the quantum yields result in a calculated photostationary composition which is significantly different from the observed one. Thus, it is clear that at least the two-bond one-photon isomerization **tc → ct** has a nonzero quantum yield.

Table II. Photostationary State Composition for 3,5-Heptadienone the in Presence of High-Energy Triplet Sensitizers[a]

	% tt	% tc	% ct
Obsd[b]	45.7	24.5	29.7
Calcd[c]	45.3	24.8	29.6

[a] Solvent is degassed benzene. [b] Based on 21 determinations using seven different sensitizers of triplet energies between 61 and 70 kcal/mol. Uncertainties at the 99% confidence level range from ±1.6 to ±0.9%. [c] See ref 2 eq 5.

The quantum yield data show that transfer of triplet energy from a sensitizer to 3,5-heptadienone isomers does not directly produce a triplet which is common to all isomers. This would require that $\Sigma\phi$ 2.00[1,2,4] and that $\phi_{tc\to tt} = \phi_{ct\to tt}$, $\phi_{tt\to tc} = \phi_{ct\to tc}$, and $\phi_{tt\to ct} = \phi_{tc\to ct}$.[4] The fact that most of the quantum yields for sensitized isomerization are smaller than those for unsensitized isomerization shows that the latter is mainly a singlet process. The simplest model for interpretation of all our dienone photoisomerization data is one in which planar or singly twisted[1,2] singlets and triplets are interconverted at rates (k_i) which are similar to their rates of decay to ground-state isomers (k_d). Neither singlets nor triplets emit, so k_d represents radiationless decay. Since singlet isomerization is more efficient than triplet isomerization, the "ratio" k_i/k_d must be larger for the singlet.

Lack of intersystem crossing and relatively efficient internal conversion from S_1 to S_0 differentiates 3,5-heptadienone from more rigid unsaturated ketones such as aromatic ketones,[10] cyclic enones,[11] and 2,5-cyclohexadienones.[12] Cyclic conjugated dienones appear to be borderline compounds. The 2,4-cycloheptadienone derivative eucarvone rearranges *ca.* 60% *via* singlets and 40% *via* triplets[13] and existing evidence indicates that polyalkyl 2,4-cyclohexadienones rear-

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(4) J. Saltiel, L. Metts, and M. Wrighton, *J. Amer. Chem. Soc.*, **91**, 5684 (1969).

(5) Dienone samples were distilled before use. The isomeric purity was greater than 99.9% (vpc) in every case. Quantum yield and actinometry samples were placed in Pyrex tubes, degassed by three freeze–pump–thaw cycles, and sealed with a flame. *n*-Hexadecane was used as an internal vpc standard. Analyses indicated no loss of dienone during irradiation.

(6) We calculate that self quenching of Michler's ketone[7] is 600 times slower than transfer of triplet energy to the dienone under our conditions.

(7) T. H. Koch and A. H. Jones, *J. Amer. Chem. Soc.*, **92**, 7503 (1970).

(8) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(9) P. S. Engel and B. M. Monroe, *Advan. Photochem.*, **8**, 245 (1971).

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(11) *Cf.* P. de Mayo, *Accounts Chem. Res.*, **4**, 41 (1971).

(12) H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, **86**, 947 (1964); *ibid.*, **89**, 906 (1967); D. J. Patel and D. I. Schuster, *ibid.*, **89**, 184 (1967).

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range in polar media *via* singlet excited states.[14] Comparison of 2,4-heptadienone with conjugated dienes, the only highly flexible compounds whose excited states are characterized in comparable detail, reveals that lack of intersystem crossing and efficient internal conversion from S_1 to S_0 are common features. Possibly the wealth of vibrational modes in S_1 allows internal conversion and isomerization to compete effectively with intersystem crossing. A striking difference between dienes and dienones is the low efficiency of triplet isomerization for dienones.

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Magnesium Ion Catalysis of the Hydrolysis of Phenyl Phosphosulfate in Acetonitrile–Water Mixed Solvent

Sir:

Magnesium ion is an essential cofactor in enzymatic reactions of 3′-phosphoadenosine 5′-phosphosulfate which acts as a sulfate group donor to numerous phenols, steroids, and carbohydrates, etc.[1] However, in nonenzymatic hydrolysis of phenyl phosphosulfate (PPS) in water, essentially no magnesium ion catalysis was detected.[2] The effects of metal ion on nonenzymatic polyphosphate hydrolysis have also been extensively studied but the catalysis observed is not large.[3] Rate acceleration has been observed only in the hydrolysis of esters which have a neighboring functional group for chelation with metal ions.[4]

For an efficient catalysis to occur, a metal ion and phosphate (or sulfate) must form a complex. This would be, however, an unfavorable process in water because of favored hydration of the metal ion and ester, whereas, in an enzymatic reaction, the medium at the active site is not necessarily water but rather would be hydrophobic in favor of metal ion–substrate binding. We now report that the magnesium ion catalyzed hydrolysis of PPS is highly sensitive to the water content of an acetonitrile–water mixed solvent.[5]

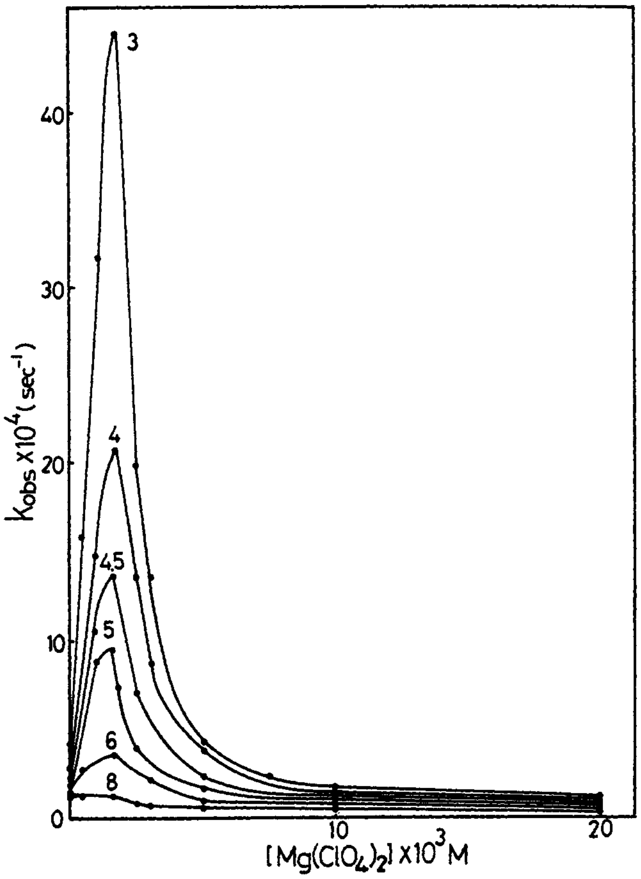

Figure 1. Effect of magnesium ion on the hydrolysis of phenyl phosphosulfate (PPS): [PPS] = 1.8×10^{-3} *M;* [$HClO_4$] = 1.0×10^{-3} *M;* [n-$Bu_4N^+ClO_4^-$] = 0.02 *M;* 25°. The numbers in the plots are the molar concentrations of water in acetonitrile–water mixed solvent.

The hydrolysis of the diammonium salt of PPS has been carried out in acetonitrile–water containing tetra-*n*-butylammonium perchlorate as the buffer reagent, and magnesium perchlorate and perchloric acid as the catalysts. Most reaction mixtures were homogeneous during the reaction, although, in the solvents of low water content (less than 3 *M*), ammonium sulfate occasionally precipitated out at the end of the reaction. The rate of reaction was followed spectrophotometrically by quenching the reaction mixture with aqueous sodium hydroxide according to the previous method[2] except for centrifugation of the quenched solutions to remove magnesium hydroxide.[6] The results are shown in Figure 1. (1) The rate acceleration by magnesium ion is not observable when the water content of the medium exceeds 8 *M;* rather, the addition of magnesium ion tends to inhibit the acid catalysis (shown by intercepts). (2) A large rate acceleration takes place in a medium of low water content showing a maximum in each plot of k_{obsd} *vs.* [$Mg(ClO_4)_2$] where the concentration of magnesium ion is very close to the initial concentration of the substrate ([PPS] = 1.8×10^{-3} *M*).[7] For example, in the solvent of [H_2O] = 3 *M*, the k_{obsd} at the maximum ($k_{max} = 4.45 \times 10^{-3}$ sec^{-1}) is ten times larger than the k_{obsd} in the absence of

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(3) B. S. Cooperman, *Biochemistry*, **8**, 5005 (1969), and references therein.

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(5) A model reaction of hydrolytic enzymes has also been examined in acetonitrile of low water content: G. Wallerberg, J. Boger, and P. Haake, *J. Amer. Chem. Soc.*, **93**, 4938 (1971).

(6) Good pseudo-first-order rate constants were obtained up to 90% completion of the reaction, in the range of [$HClO_4$] = 0.3–3.0 $\times 10^{-3}$ *M*, both in the presence and absence of $Mg(ClO_4)_2$, although significant deviation from the first-order kinetics due to autocatalytic rate acceleration was observed below [$HClO_4$] = 0.3×10^{-3} *M*. The rates were invariant to the change of salt (n-$Bu_4{}^+NClO_4{}^-$) concentration from 0.02 to 0.2 *M* for all the mixed solvents as well as pure water (see also p 4973 in ref 2a). Hydrolysis of neither the product (phosphate) nor solvent (acetonitrile) was detected.

(7) Similar curves were also observed when [$HClO_4$] = 0.5×10^{-3} *M*.