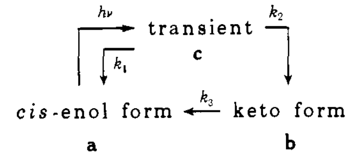
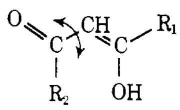
the enol **a** and the ketone **b** while the transients of the β-diketones **3–7** convert only to the corresponding *cis*-enol forms **a**.

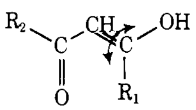
These results may be rationalized by Scheme I, in

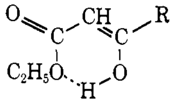
Scheme I



which k_1–k_3 denote the rate constants for the dark reactions. Two structures, A and B, in which the hydrogen bond of the *cis*-enol **a** is opened, may be proposed for these transients: structure A, having an s-trans arrangement of the α,β-unsaturated keto chromophore and derived from the enol form **a** by rotation around the CO—C single bond, and structure B, having an s-cis arrangement and derived by rotation around the C=C double bond.[3] We prefer structure A since it


A


B


C

explains the facile reconversion of the transient into the starting *cis*-enol by rotation around the "single" bond. If B were the correct structure, this enol–enol interconversion would involve rotation around the C=C double bond, and one might expect[5] an activation energy of at least 25 kcal, and therefore a decay predominantly to the keto form.

In the β-diketones the enol–enol interconversion (k_1) is faster than the alternative ketonization (k_2) which latter involves an intermolecular hydrogen transfer from oxygen to carbon. However, triethylamine greatly enhances this hydrogen transfer process.

In the β-keto esters the corresponding transient enol C is probably stabilized by hydrogen bonding involving the ether oxygen. This may be expected to enhance the energy barrier of rotation around the single bond and decrease k_1, thereby favoring the alternative ketonization process k_2.

[3] The photoisomerization of diaroyl acetates described recently[4] may be explained by a similar mechanism.

[4] P. Courtot and S. Y. Le Saint, *Tetrahedron Lett.*, 33 (1973).

[5] Y. Shvo, E. C. Taylor, and Y. Bartuliu, *Tetrahedron Lett.*, 3259 (1967).

[6] (a) Department of Organic Chemistry; (b) Department of Structural Chemistry.

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Electron Spin Resonance Study of Allylic Monomer Radical Formation from Tetramethylethylene Dimer Radical Cation Due to Intramolecular Proton Transfer in γ-Irradiated 3-Methylpentane Glasses

Sir:

It has been shown by means of esr that γ-irradiated 3-methylpentane (3-MP) glasses containing small amounts of tetramethylethylene (TME) produce the solute radical cations at 77°K.[1] At high solute concentrations the dimer radical cation $(\text{TME})_2^+$ has been found to be formed. In the present work, we wish to report that the dimer cation produced changes into the allylic monomer radical $\dot{C}H_2(CH_3)C{=}C(CH_3)_2$ at 77°K in the dark, which suggests allyl radical formation through intramolecular proton transfer of the dimer cation.

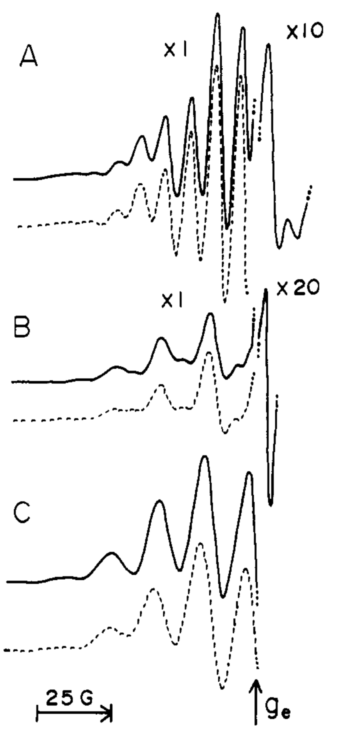

Figure 1. Low field sides of esr spectra (solid line) of 3-MP glasses containing 10 mol % TME: (A) 0.2 mol % CO_2 present, measured 20 min after irradiation; (B) same as A but 40 days after irradiation; (C) without CO_2, 40 days after irradiation. The fields near g_e in the spectrum A and B were recorded at reduced sensitivities. Dotted lines show the computed spectra consisting of the lines from the paramagnetic species: (A) $(\text{TME})_2^+$ (55%) and 3-MP radical (45%); (B) $(\text{TME})_2^+$ (10%), R_a (80%), and 3-MP radical (10%); (C) R_a (90%) and 3-MP radical (10%).

Samples prepared from purified materials were cooled to 77°K and subjected to ^{60}Co γ-irradiation at a dose rate of 5×10^{17} eV g^{-1} min^{-1}. Esr measurements were carried out with a conventional X-band spectrometer at 77°K.

Shown in Figure 1A, by the solid line, is the low field side of the esr spectrum of 3-MP glass containing 10 mol % TME and 0.2 mol % CO_2 measured 20 min after irradiation. The spectrum was interpreted as a superposition of lines from three paramagnetic species,[1] *i.e.*, CO_2^- anions (a strong asymmetric line), 3-MP radical (broad six lines with an average spacing of 22.2 G), and $(\text{TME})_2^+$ cations (a set of 25 lines with an average spacing of 7.8 G). The observed spectrum may be compared with the composite spectrum (dotted line) which consists of a computed 3-MP radical spectrum (45%) with intensity ratios of 1:5:10:10:5:1 and a computed $(\text{TME})_2^+$ spectrum (55%) with a binominal distribution of intensity ratios; the aforementioned spacings and a Gaussian line shape were used for the

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[1] T. Ichikawa and P. K. Ludwig, *J. Amer. Chem. Soc.*, **91**, 1023 (1969).

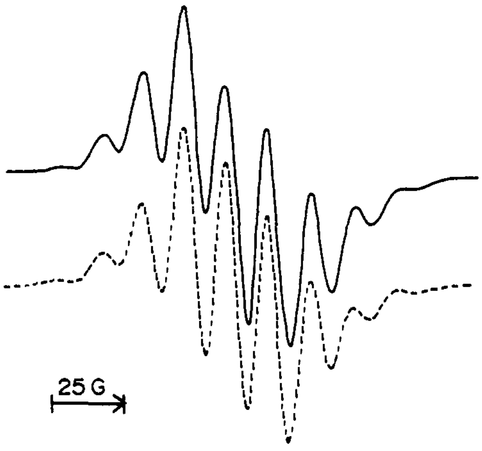
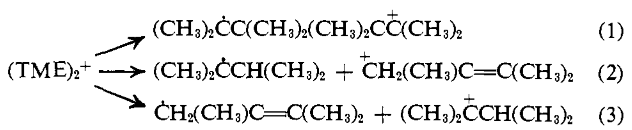


Figure 2. Esr spectrum (solid line) of 3-MP glass containing 1 mol % 1-bromo-2,3-dimethyl-2-butene measured 5 days after irradiation and the computed spectrum (dotted liine) consisting of lines from R_a (90%) and 3-MP radical (10%).

computations. It shows close agreement with the observed spectrum except near the CO_2^- line.[2] When the sample was kept at 77°K in the dark for 40 days after irradiation, the spectrum changed as shown in Figure 1B. Most of the lines due to the dimer cations and the 3-MP radicals disappeared, the asymmetric CO_2^- line grew to a symmetric line, and a nine-line spectrum with an average spacing of 13.70 ± 0.15 G appeared (radicals responsible for the spectrum are abbreviated as R_a). Formation of R_a is more clearly shown in Figure 1C which was obtained by keeping the irradiated 3-MP glass containing 10 mol % TME without CO_2 under the same conditions as those given for Figure 1B. The appropriate computed spectra for the observed spectra of Figures 1B and 1C are shown by dotted lines, respectively.

We obtained the following results for growth and decay of the paramagnetic species produced in the TME–CO_2–3-MP systems.[3] The decay of $(TME)_2^+$ closely correlates with the growth of R_a, of which the amounts become equal to those of $(TME)_2^+$ 70 ± 20 min after irradiation, and the times required for the first 50% of 3-MP radicals and the first 35% of CO_2^- are 15 ± 5 and 20 ± 5 hr, respectively. Rate constants obtained from application of the first-order kinetics for the $(TME)_2^+$ decay during the periods from 30 to 220 min and from 220 to 1800 min after irradiation are 2.9×10^{-2} and 1.6×10^{-3} min^{-1}, respectively.[4] The corresponding rate constants determined from the growth of R_a are respectively 3.3×10^{-2} and 0.99×10^{-3} min^{-1}; these values show fairly good agreement with the values obtained from the decay of $(TME)_2^+$. These results suggest that the formation of R_a is not related to the decay of 3-MP radicals nor to charge recombination processes between $(TME)_2^+$ and CO_2^-. It seems more likely that R_a is produced by an intramolecular reaction of $(TME)_2^+$.



$$(\mathrm{TME})_2^+ \longrightarrow (\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{C}(\mathrm{CH_3})_2(\mathrm{CH_3})_2\mathrm{C}\overset{+}{\mathrm{C}}(\mathrm{CH_3})_2 \tag{1}$$

$$(\mathrm{TME})_2^+ \longrightarrow (\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{CH}(\mathrm{CH_3})_2 + \overset{+}{\mathrm{C}}\mathrm{H_2}(\mathrm{CH_3})\mathrm{C}{=}\mathrm{C}(\mathrm{CH_3})_2 \tag{2}$$

$$(\mathrm{TME})_2^+ \longrightarrow \dot{\mathrm{C}}\mathrm{H_2}(\mathrm{CH_3})\mathrm{C}{=}\mathrm{C}(\mathrm{CH_3})_2 + (\mathrm{CH_3})_2\overset{+}{\mathrm{C}}\mathrm{CH}(\mathrm{CH_3})_2 \tag{3}$$

The radical responsible for the observed spectra is most likely the allylic monomer radical produced by reaction 3 which may be induced by intramolecular proton (and/or H atom) transfer. If the unpaired spin couples equally with the two protons of the methylene group and the six protons of the methyl groups bonded to the terminal carbon atom, these eight equivalent protons would give a nine-line spectrum with a binominal distribution of intensity ratios. The observed hyperfine coupling constant of 13.7 G is not an unreasonable order of magnitude for the allyl type radical.[5,6] It is to be noted that in the 3-MP or CO_2–3-MP systems containing TME at less than 0.3 mol %, the TME monomer radical cations were found to be produced instead of $(TME)_2^+$.[1] The formation of R_a was not observed in the dark during prolonged storage of the samples at 77°K.

The solid line spectrum in Figure 2 shows the esr spectrum of γ-irradiated 3-MP glass containing 1 mol % of 1-bromo-2,3-dimethyl-2-butene measured 5 days after irradiation. A nine-line spectrum with an average spacing of 14.00 ± 0.15 G superimposed on the 3-MP radical spectrum is discernible. The dotted line spectrum is a computed spectrum, which agrees quite well with the observed spectrum. This nine-line spectrum may be identified as the allylic radical produced by dissociative electron capture of the bromide.

$$\mathrm{CH_2Br(CH_3)C{=}C(CH_3)_2} + e^- \longrightarrow \dot{\mathrm{C}}\mathrm{H_2(CH_3)C{=}C(CH_3)_2} + \mathrm{Br}^- \tag{4}$$

The result provides conclusive evidence for the identification of R_a as the allylic TME monomer radical.

Ayscough and Evans[5] and Smith and Pieroni[6] found formation of allylic radicals in γ-irradiated vinylene (RCH=CHR′) or vinylidene (CH_2=CRR′) olefins at 77°K by the use of esr methods and assumed an ion–molecule reaction of the type

$$\mathrm{C}_n\mathrm{H}_{2n}^+ + \mathrm{C}_n\mathrm{H}_{2n} \longrightarrow \mathrm{C}_n\mathrm{H}_{2n-1} + \mathrm{C}_n\mathrm{H}_{2n+1}^+ \tag{5}$$

for the allylic radical formation. Shida and Hamill[7] found the reaction of this type to be endothermic for vinylene or vinylidene olefins on the basis of thermochemistry and assumed that excited cations undergo reaction 5 to yield allylic radicals. Our results indicate that a reaction of the type

$$(\mathrm{C}_n\mathrm{H}_{2n})_2^+ \longrightarrow \mathrm{C}_n\mathrm{H}_{2n-1} + \mathrm{C}_n\mathrm{H}_{2n+1}^+ \tag{6}$$

would possibly contribute to the formation of allylic radicals in solid-phase radiolysis of vinylene or vinylidene olefins. Although direct evidence for the presence of the monomer cation $(CH_3)_2C^+CH(CH_3)_2$ was not obtained, finding of the conversion of $(TME)_2^+$ to the allylic monomer radical strongly suggests the presence of the monomer cation in the vicinity of R_a. The

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(2) The small discrepancy between the observed spectrum and the calculated one is due to superposition of lines from the allylic radicals already converted from $(TME)_2^+$. A recalculated spectrum consisting of lines from 37.5% of the dimer cations, 17.5% of the allylic radicals, and 45% of the 3-MP radicals showed better fitting with the observed spectrum.

(3) The decay and growth curves of the component radicals from 20 min to 40 days after irradiation which are not presented in the text were obtained from the relative yields determined from comparison of the observed spectra with the computed ones.

(4) The fast and slow decay rates obtained may be considered to be caused by the differences of environments of the trapped dimer cations, since the TME molecules do not dissolve homogeneously at 77°K in the 3-MP matrix at high concentrations.

(5) P. B. Ayscough and H. E. Evans, *Trans. Faraday Soc.*, 60, 801 (1964).

(6) D. R. Smith and J. J. Pieroni, *J. Phys. Chem.*, 70, 2379 (1966).

(7) T. Shida and W. H. Hamill, *J. Amer. Chem. Soc.*, **88**, 5376 (1966).

hyperfine coupling constant of R_a from $(TME)_2^+$, however, is slightly lower than that of R_a from the bromide within the limit of accuracy. This might be caused by delocalization of the unpaired electron of R_a to the neighboring monomer cation such as by charge-transfer mechanism.

Acknowledgment. We wish to express appreciation to Professor Masaji Miura and Doctor Akinori Hasegawa for use of an esr spectrometer.

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Received September 10, 1973

Low-Temperature Polarized Spectral Study of the Lowest Electronic Absorption Band in $Re_2Cl_8^{2-}$ and Related Binuclear Complexes

Sir:

Quadruple metal–metal bonding is well established for the ground state of the D_{4h} $Re_2Cl_8^{2-}$ complex. Properties such as diamagnetism, a very short (2.24 Å) Re–Re bond length, and an eclipsed rotational configuration of attached $ReCl_4^-$ units all point to a $^1A_{1g}$ ground-state electronic structure in which the eight d valence electrons furnished by the two Re(III) units occupy metal–metal bonding molecular orbitals of $a_{1g}\sigma$, $e_u\pi$, and $b_{2g}\delta$ symmetries.[1] The molecular orbitals that are occupied in the lowest electronic excited states are much less certain. Extended Hückel MO calculations predict that the lowest spin-allowed electronic transitions in $Re_2Cl_8^{2-}$ are $^1A_{1g} \rightarrow {}^1B_{1u}$ $(b_{2g}\delta \rightarrow a_{2u}\sigma_n)$ and $^1A_{1g} \rightarrow {}^1A_{2u}$ $(b_{2g}\delta \rightarrow b_{1u}\delta^*)$.[2] $^1A_{1g} \rightarrow {}^1B_{1u}$, which is orbitally forbidden, was calculated[2] to fall at slightly lower energy than the z-allowed $^1A_{1g} \rightarrow {}^1A_{2u}$ transition.

The electronic absorption spectrum of $Re_2Cl_8^{2-}$ in methanol solution exhibits bands at 14.5 (f = 0.023), 32.8 (f = 0.31), and 39.2 kcm^{-1} (f = 0.65).[3] Arguing that an f value of 0.023 is too low for an allowed transition of the $\delta \rightarrow \delta^*$ type, Cotton assigned[4] the 14.5-kcm^{-1} band to a $\delta \rightarrow \sigma_n$ (specified[2] later as $^1A_{1g} \rightarrow {}^1B_{1u}$) transition. The fact that the band in question is either shifted substantially or absent in the electronic spectra[5] of binuclear complexes such as $Re_2(O_2CC_3H_7)_4Cl_2$, which have axially coordinated groups, was cited[2,4] in support of the $\delta \rightarrow \sigma_n$ assignment. However, we would expect both σ_n and δ^* orbitals to be destabilized in axially bonded complexes in which the metal is forced to lie approximately in the plane of the equatorial donor atoms. In order to provide additional evidence on which to base electronic structural discussion, we have measured the MCD and 5°K polarized electronic spectra of several binuclear Re(III) complexes. These studies have established that the low-energy band system in $Re_2Cl_8^{2-}$ and closely related dimers arises from the $\delta \rightarrow \delta^*$ transition, as reported herein.

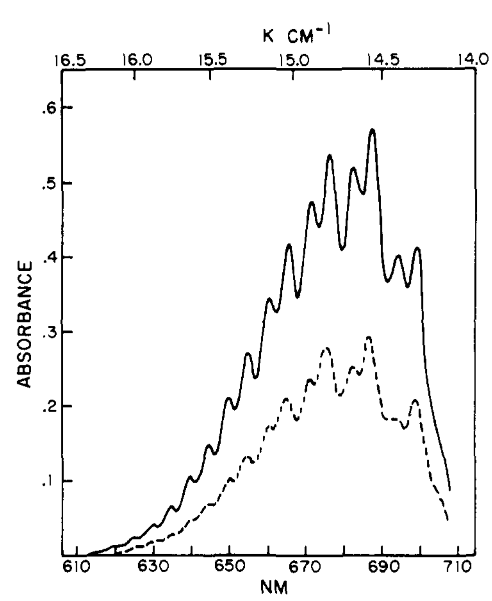

Figure 1. Parallel (—) and perpendicular (----) polarized absorption spectra on (100) of a single crystal of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$.

Table I. Vibrational Structure of the 14,183-cm^{-1} Band in $Re_2Cl_8^{2-}$ at 5°K

nm	cm^{-1}	$\Delta\bar{\nu}$(a), cm^{-1}	$\Delta\bar{\nu}$(b), cm^{-1}	Assignment
705.06 (10)	14,183 (2)	0	0	Origin
699.41	14,298		115	$a_{1g}(\nu_3)$
694.12	14,407	224		$a_{1g}(\nu_2)$
687.65	14,542		245	$\nu_3 + \nu_2$
682.41	14,654	247		$2\nu_2$
676.24	14,788		245	$\nu_3 + 2\nu_2$
671.00	14,903	249		$3\nu_2$
665.06	15,036		249	$\nu_3 + 3\nu_2$
660.00	15,152	248		$4\nu_2$
654.35	15,282		246	$\nu_3 + 4\nu_2$
649.29	15,401	250		$5\nu_2$
644.12	15,525		243	$\nu_3 + 5\nu_2$
639.00	15,649	248		$6\nu_2$
634.29	15,766		240	$\nu_3 + 6\nu_2$

The 5°K polarized spectra of a thin crystal of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ between 710 and 600 nm are shown in Figure 1.[6] The observed vibrational structure is assigned in Table I. A prominent progression in the a_{1g}-(ν_2) Re–Re stretching vibration (average spacing 248 cm^{-1}, ground state[7] 274 cm^{-1}) is built on an electronic origin at 14,183 cm^{-1}. A slightly weaker, second progression (average spacing 245 cm^{-1}) of $a_{1g}(\nu_2)$ begins at 14,298 cm^{-1}. The 115-cm^{-1} separation of the two progressions corresponds to the excitation of one quantum of $a_{1g}(\nu_3)$, the totally symmetric ReReCl bending mode (ground state[7] 115 cm^{-1}). At 77°K a single vibrational progression is observed with an average spacing of 254

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(1) F. A. Cotton, *Accounts Chem. Res.*, **2**, 240 (1969); and references therein.

(2) F. A. Cotton and C. G. Harris, *Inorg. Chem.*, **6**, 924 (1967).

(3) F. A. Cotton, N. F. Curtis, B. F. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4**, 326 (1965).

(4) F. A. Cotton, *Inorg. Chem.*, **4**, 334 (1965).

(5) F. A. Cotton, C. Oldham, and W. R. Robinson, *Inorg. Chem.*, **5**, 1798 (1966).

(6) The $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ complex was prepared by a literature method.[3] An X-ray examination showed that the compound crystallizes in the space group $P2_1/_c$ with a = 10.91, b = 15.34, and c = 16.43 Å, and β = 122.66°. For two $Re_2Cl_8^{2-}$ anions per unit cell, the calculated density is 1.635 g/cm^3. The density determined by flotation in bromoform–carbon tetrachloride is 1.623 g/cm^3. For the spectral studies, thin single crystals were grown from acetonitrile on quartz substrates. Spectral data were obtained using a Cary 17 spectrophotometer equipped with an Andonian liquid helium dewar and double Glan-Taylor air-spaced calcite polarizers. Spectra were measured along the extinction directions of the (100) crystal face.

(7) W. K. Bratton, F. A. Cotton, M. Debeau, and R. A. Walton, *J. Coord. Chem.*, **1**, 121 (1971).