rounding each metal ion are identical, one may demonstrate that there is a definite maximum limit to the valence delocalization which is compatible with the existence of two sites with differing nuclear configurations. Using the spectral data of Creutz and Taube[1] we can then show that the extent of valence delocalization in compound I lies well below this limit.

For a class II system regarded formally as $A^{X+}\ B^{Y+}$ the ground state may be written

$$\Psi_G = [\Psi(A^{X+}B^{Y+}) + \alpha\Psi(A^{Y+}B^{X+})]/\sqrt{1 - \alpha^2} \quad (4)$$

and the excited state

$$\Psi_{MV} = [\Psi(A^{Y+}B^{X+}) - \alpha'\Psi(A^{X+}B^{Y+})]/\sqrt{1 - \alpha^2} \quad (5)$$

The dipole length transition moment governing the spectral intensity of the transition $\Psi_G \rightarrow \Psi_{MV}$ is

$$\mu = {}^1/_2(\alpha + \alpha')R_{AB} \quad (6)$$

R_{AB} is the distance separating the two centers A and B, and α and α' are given by first-order perturbation theory as

$$\alpha = \beta/(E_{MV} - E_G) \quad (7a)$$

$$\alpha' = \beta'/(E_{MV} - E_G) \quad (7b)$$

where $(E_{MV} - E_G)$ is approximately equal to the energy of the mixed-valence absorption band, while β and β' are resonance energies in the ground and excited states, respectively. Since $\Psi(A^{X+}B^{Y+})$ and $\Psi(A^{Y+}B^{X+})$ are effectively orthogonal when A and B are well separated, they may interact only *via* mutually nonorthogonal A → (ligand)*, (ligand) → B charge-transfer states. This situation is quite analogous to that occurring in the theory of superexchange.[7] Since the metal–ligand charge-transfer states are closer in energy to Ψ_{MV} than to Ψ_G, perturbation theory yields the result $\beta' > \beta$, $\alpha' > \alpha$. The experimentally observed quantity $(\alpha + \alpha')/2$ is then greater than α, which in turn equals β/E_{FC} (eq 7a). However, for trapping of valence, $\beta < E_{FC}/4$, so that

$$\alpha < 1/4 \quad (8)$$

In a class III system $\alpha^2 = 0.5$ so that any experimentally determined value of α^2 between 0.07 and 0.5 would invalidate the valence-trapping criterion suggested above.

From the data of Taube and Creutz[1] the transition dipole μ of the mixed-valence band in I may be estimated at roughly 1.07 eÅ, yielding a value of about 0.15 for $^1/_2(\alpha + \alpha')$. Thus $\alpha^2 \leqslant 0.025$, which satisfies the criterion for trapping (8). From the same data a resonance integral for valence interaction at the point $x = 0$ in the energy surface of Figure 1 may be estimated as $\beta \leqslant 975$ cm^{-1} (0.12 eV). Resonance interaction H_{res} at the point $x = {}^1/_2$ will be of similar magnitude, and the energy of adiabatic charge-transfer E_{Ad} is 1625 cm^{-1}.

We can also show that our estimate of the resonance integral β is realistic by another simple theoretical approach. If the states $\Psi[Ru_A^{2+}Ru_B^{3+}]$ and $\Psi[Ru_A^{3+}Ru_B^{3+}]$ are considered to be orthogonal, interacting only by a second-order mechanism involving nonorthogonal ligand $\pi \rightarrow Ru^{3+}$ and $Ru^{2+} \rightarrow$ ligand π^* charge-transfer states,[8] the resonance integral β is given by perturbation theory as

$$\beta = \sum_i \frac{\langle\Psi_0|H|\Psi_{CTi}\rangle\langle\Psi_{CTi}|H|\Psi_{CT}\rangle}{E_{CTi} - E_0}$$

where $\Psi_0 = \Psi[Ru_A^{2+}Ru_B^{3+}]$, $\Psi_{CT} = [Ru_A^{3+}Ru_B^{2+}]$, and Ψ_{CTi} are all other ligand $\pi \rightarrow Ru^{3+}$, $Ru^{2+} \rightarrow$ ligand π^* charge-transfer states; β' is given by a similar expression having denominator $(E_{CTi} - E_{CT})$. The integrals defining β may be estimated semiempirically from the energies and intensities of observed metal(II) → ligand π^* and ligand π → metal(III) charge-transfer bands. We have employed the method used by Sanders and Day[9] in the assignment of the charge-transfer spectra of iron complexes with conjugated ligands. The value of β calculated by this method is 1040 cm^{-1}. This estimate involves the assumption that the unpaired electron density in the Ru(III) d^5 system is distributed almost equally over the d_{xy}, d_{xz}, d_{yz} orbitals, which seems reasonable in view of the high spin–orbit coupling constant for Ru(III) (1000 cm^{-1} [10]) and the similar ligand field strengths of ammonia and pyrazine.[10] Such a distribution of spin-unpaired electron density gives a good agreement between calculated and observed intensities for the ligand $\pi \rightarrow$ Ru(III) charge-transfer absorption at 28.5 kK in the (III,III) complex when $\beta_{Ru(III)N}$ is set equal to $\beta_{Ru(II)N}$. Using our calculated values of β and β' we estimate the transition dipole of the mixed-valence absorption band as 1.4 eÅ. The observed value is 1.07 eÅ.

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[7] P. W. Anderson, *Phys. Rev.*, **79**, 350 (1950).

[8] B. Mayoh and P. Day, to be published.

[9] N. Sanders and P. Day, *J. Chem. Soc. A*, 1191 (1970); 2303 (1969); 1530, 1536 (1967).

[10] B. N. Figgis, "An Introduction to Ligand Fields," Wiley, New York, N. Y., 1966.

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Thermal Decomposition of Tetramethyl-1,2-dioxetane. Selective and Efficient Chemelectronic Generation of Triplet Acetone[1]

Sir:

The mechanism of production and the nature of electronically excited state(s) involved in chemelectronic reactions (*i.e.*, reactions in which at least one elementary step involves the conversion of chemical energy into electronic excitation energy) are of great interest to kineticists,[2] biochemists,[3] and photochemists.[4]

The involvement of an oxygen molecule, or its equivalent (*e.g.*, a peroxide), in bioluminescent systems[5] and the probable involvement of singlet oxygen[6] in many reactions which are chemiluminescent, has led to the postulate of 1,2-dioxetanes as reaction intermedi-

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[1] Molecular Photochemistry. LII. Paper LI: N. J. Turro, *et al.*, *J. Amer. Chem. Soc.*, **94**, 1392 (1972). The authors thank the Air Force Office of Scientific Research (Grant AFOSR-70-1848) and the National Science Foundation (Grant No. GP-26602x) for their generous support of this work.

[2] R. F. Vassilev, *Progr. React. Kinet.*, **4**, 305 (1967); *Russ. Chem. Rev.*, **39**, 529 (1970).

[3] F. H. Johnson and Y. Haneda, "Bioluminescence in Progress," Princeton University Press, Princeton, N. J., 1966.

[4] E. H. White, J. Wiecko, and D. Roswell, *J. Amer. Chem. Soc.*, **91**, 5194 (1969); H. E. Zimmerman, D. Dopp, and P. S. Huyffer, *ibid.*, **88**, 5352 (1966).

[5] T. Gato, *Pure Appl. Chem.*, **17**, 421 (1968).

[6] F. McCapra and R A. Hahn, *J. Chem. Soc. D*, 442 (1969).

Table I. Efficiencies at 70° for Production of Singlet and Triplet Acetone per Molecule of **1** Decomposed[a]

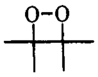
Method	[Dioxetane], *M*	[Quencher], *M*	Solvent	ϕ(chem), %[c] Oxetane	ϕ(chem), %[c] Isomerization	ϕ(photochem), % Oxetane	ϕ(photochem), % Isomerization	ϕ(excited), % Singlet	ϕ(excited), % Triplet[d]
t-DCE[b]	1.07	1.30	Benzene	0.022	4.8	8	10	0.28	48
c-DEE[b]	0.71	1.07	CH_3CN	<0.01	8.8	10	30	<0.1	30
Actinometry[e]	0.1		Benzene					0.16	
Biacetyl[f]	0.02		Benzene					0.8	50

[a] Thermal decomposition of **1** at 70° in benzene. It follows first-order kinetics ($k = 4.05 \times 10^{-4}$ sec^{-1} at 71°). The same rate is found for decomposition of **1** and disappearance of chemiluminescence at the maximum 404 nm. Error limits are estimated to be of the order of ±50%. [b] Actual runs. Variation of the concentration ratio [dioxetane]/[quencher] from 2:1 to 1:2 had no significant effect. Averages: 0.2% singlet, 50% triplet per mole of dioxetane decomposed. [c] Product formation per mole of dioxetane decomposed. Singlets form oxetanes, triplets give rise to isomerization. [d] ϕ(excited) = ϕ(chem)/ϕ(photochem). [e] Absolute actinometry, using ferrioxalate. See J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, **75**, 991 (1971). [f] Extrapolated to infinite concentration of biacetyl.

ates.[7] We report here a quantitative study of the decomposition of tetramethyl-1,2-dioxetane (**1**) and present evidence that, in the thermolysis of **1** to 2 mol of acetone, **1** *efficiently and selectively yields acetone triplets which are not generated from acetone singlet precursors.*

Following Kopecky and Mumford's[8] pioneering synthesis of the first well-characterized 1,2-dioxetane, many papers have appeared concerned with the syntheses and investigation of this fascinating family of high-energy content small ring compounds.[9] White, *et al.*,[10] have reported that **2** yields as high as about 5% of an active species capable of sensitizing reactions (characteristic of triplet photochemistry) of suitable acceptors. Wilson and Schaap[11] suggested that **3** may yield ethyl formate triplets (presumably *via* ethyl formate singlet precursors) in high, possibly quantitative, yield. Güsten and Ullman[12] suggested that **4** can sensitize reactions with an efficiency approaching 5% in favorable cases. In none of these cases has the chemelectronically formed excited species been unambiguously defined.[10b]

The reactions of singlet and triplet acetone with *trans*-1,2-dicyanoethylene (*t*-DCE) yield oxetane **5** and *cis*-1,2-dicyanoethylene (*c*-DEE), respectively, as the exclusive products.[13] The photochemical mechanisms of these reactions have been studied in detail, are thought to be well understood, and are relatively insensitive to solvent and temperature.[13,14] Thus, the thermal decomposition of **1** in the presence of *t*-DCE was chosen as a system in which, at the same time, we could chemically titrate both the number of moles of excited singlet acetone (^{1}A) and triplet acetone (^{3}A) produced per mole of **1** decomposed. Knowing the limiting quantum yields for formation of (a) **5** from ^{1}A and *t*-DCE, and (b) *c*-DCE from ^{3}A and *t*-DCE, we can easily measure the limiting yields of ^{1}A and ^{3}A produced from thermolysis of **1**.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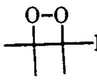
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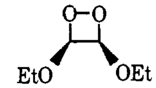
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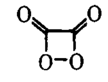
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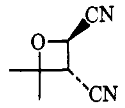
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Our results are summarized in Table I. To our surprise, based on titration by *t*-DCE, *the yield of ^1A was less than 1%, while the yield of ^3A was about 50%!* Since this result was unexpected, we sought other independent and unambiguous checks for titrating ^{1}A and ^{3}A. Indeed, we found (Table I) that the same yields of ^{3}A and ^{1}A were obtained, within experimental error, by absolute measurement of the chemiluminescence (pure acetone fluorescence) of **1**, by sensitization of biacetyl fluorescence and phosphorescence, and by chemical titration with *cis*-1,2-diethoxyethylene (*c*-DEE).

Furthermore, we found that Stern–Volmer quenching of the chemiluminescence of **1** by *t*-DCE (benzene solution) yields a $k_q\tau$ value identical with that for quenching of acetone fluorescence by *t*-DCE. Finally, thermolysis of **1** in the presence of norbornene yields norbornene dimers. This dimerization is known to be triplet sensitized only if E_3 (sensitizer) is >70 kcal.[15] Taken as a whole, these data add up to a strong case for the facile, selective, and efficient thermolysis of **1** into triplet acetone, with only minor formation of singlet acetone.

Incidental to this study we noticed that high concentration of **1** decreases the net yield of ^{3}A, indicating that **1** is a quencher[16] of ^{3}A. Consistent with this possibility is the observation that degassed solutions show less chemiluminescence then aerated solutions.[17] We interpret this result as follows: since oxygen is known to be an efficient quencher[18] of ^{3}A but not ^{1}A, oxygen protects **1** against sensitized decomposition by ^{3}A (which apparently does not generate ^{1}A), thereby allowing more molecules of **1** to form ^{1}A (the state responsible for chemiluminescence).

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(7) F. McCapra, *Chem. Commun.*, 155 (1968); E. H. White and M. J. C. Harding, *J. Amer. Chem. Soc.*, **86**, 5686 (1964).

(8) K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969).

(9) H. E. O'Neal and W. H. Richardson, *J. Amer. Chem. Soc.*, **92**, 6553 (1970), and references therein.

(10) (a) E. H. White, J. Wiecko, and C. C. Wei, *ibid.*, **92**, 2167 (1970); comparable efficiency was noted by A. A. Lamola, *Biochem. Biophys. Res. Commun.*, **40**, 304 (1971). (b) Triplet states were clearly indicated, but it was not established whether acetone or acetaldehyde (or a mix) triplets were involved.

(11) T. Wilson and R. P. Schaap, *J. Amer. Chem. Soc.*, **93**, 4126 (1971).

(12) H. Güsten and E. F. Ullman, *J. Chem. Soc. D*, 28 (1970).

(13) J. C. Dalton, P. A. Wriede, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 1318 (1970).

(14) J. C. Dalton, P. A. Wriede, and G. Kavarnos, unpublished results.

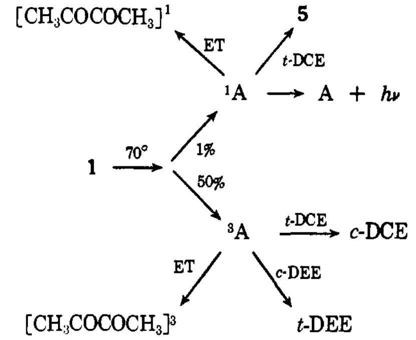
(15) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968).

(16) Wilson and Schaap report a related observation. They showed that **3** quenches the fluorescence of anthracene triplets. See ref 11.

(17) **1** quenches biacetyl phosphorescence with $k_q \sim 10^7$ M^{-1} sec^{-1}.

(18) For example, the fluorescence yield of acetone is the same in aerated or degassed solution [R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966)], but triplet reactions of acetone are expected to be quenched by aeration.

Scheme I



We summarize our findings in Scheme I. In addition to the remarkably efficient and selective[19] formation of ^3A relative to ^1A, we wish to point out that the blue (acetone fluorescence) chemiluminescence is a "red herring" with respect to the major method for excited state production from **1**. This shows the hazards of making mechanistic conclusions solely on the basis of low-efficiency chemiluminescence. Finally, **1** is a "self-quencher" of chemelectronic production of ^3A, while dissolved oxygen is a "promoter" of chemiluminescence. We conclude that low concentrations of **1** in the absence of oxygen (*i.e.*, under conditions that chemiluminescence is *decreased*) are most favorable for efficient production of chemically useful excited states (triplets) from **1**.

Acknowledgments. The authors thank Mr. Mark P. Niemczyk for his assistance in the early phases of this work. Special thanks are extended to Professor Karl Kopecky for kindly providing us with a detailed procedure for the preparation of **1**. We also thank Professor David Kearns for a helpful discussion of the mechanism of dioxetane decomposition.

[19] Although we are not in a position yet to make a distinction between a multistep or concerted production of ^3A, we point out that Kearns has calculated that the energy of passing from 1 to ^3A might be lower than from 1 to ^1A: *J. Amer. Chem. Soc.*, **91**, 6554 (1969).

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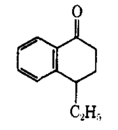
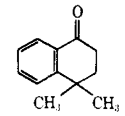
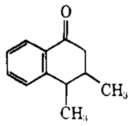
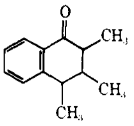
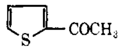
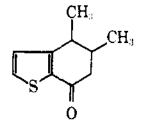
Oxidation by Metal Salts. IX. Formation of Cyclic Ketones

Sir:

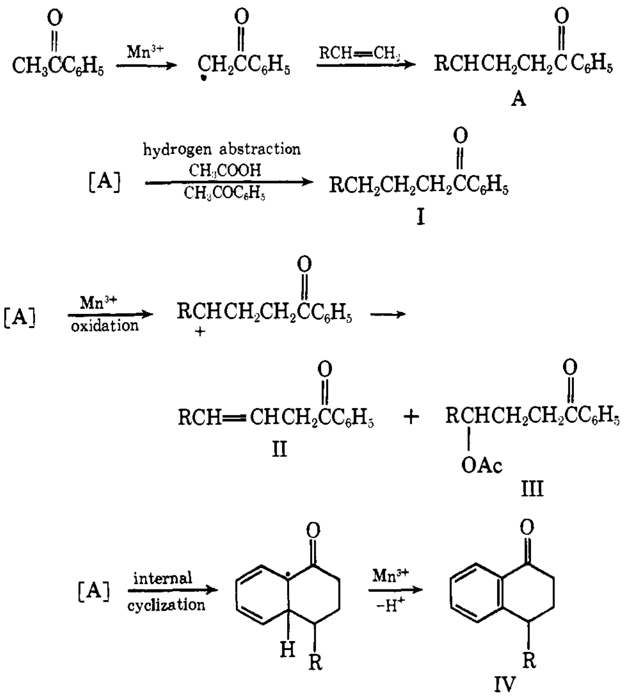
In an earlier communication[1] we described a reaction of olefins with aliphatic ketones in the presence of manganic and ceric acetates, which led to the formation of three major products: saturated ketone I, unsaturated ketone II, and keto acetate III. We have now found that when an aromatic ketone such as acetophenone was used, a new fourth product, α-tetralone IV, was obtained as the predominant product in about 50% yield[2] (Table I).

Table I. Yields of Cyclic Ketones

Ketone	Olefin	Cyclic ketone	Yield (based on Mn^{3+}), %
$C_6H_5COCH_3$	Butene-1		49
	Isobutylene		43
	Butene-2		40
	Butene-2		53
	Butene-2		43

The formation of these cyclic ketones together with the three noncyclic products can best be explained by the mechanism shown below (Scheme I). As shown, the radical intermediate A undergoes three competing reactions: (1) hydrogen abstraction from the solvent, (2) oxidation by the higher valent metal ion, and (3) internal cyclization. The ratio of tetralone IV ($R_1 =$ C_2H_5; $R_2 =$ H) to saturated ketone I (15, at 1.35 *M* acetophenone) was independent of the nature or concentration of the metal ion used and decreased as the acetophenone concentration increased. The ratio of tetralone IV to the oxidation products II and III, how-

Scheme I



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[1] E. I. Heiba and R. M. Dessau, *J. Amer. Chem. Soc.*, **93**, 524 (1971).

[2] Yield is based on the requirement of 2 equiv of metal ion/mol of tetralone.