

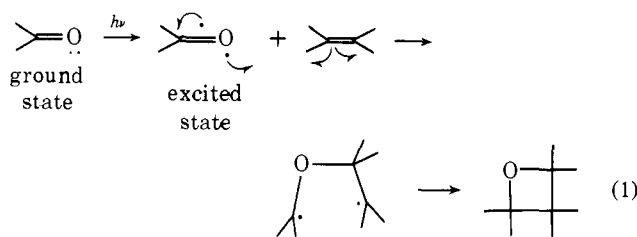
# Mechanism of the Interaction of $n, \pi^*$ Excited Alkanones with Electron-Rich Ethylenes

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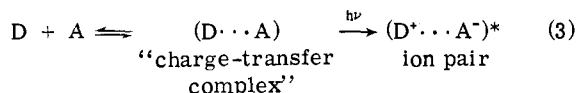
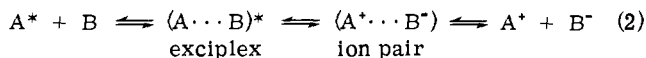
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**Abstract:** The results of luminescence-quenching experiments involving both singlet and triplet  $n, \pi^*$  ketones and electron-rich ethylenes are described. Quenching rate constants for norcamphor fluorescence, acetone fluorescence and phosphorescence, and benzophenone phosphorescence are reported for a number of mono- and dialkoxyethylenes and are found to correlate well with TCNE charge-transfer data and gas-phase ionization potentials of the alkenes. A quenching mechanism is proposed that involves formation of an excited-state complex (exciplex) which partitions either to regenerate ground states or to yield biradicals which may go on further to form oxetanes. Plots of  $\log k_q$  vs. adiabatic ionization potential show slopes of  $-1.5/\text{eV}$  to  $-2/\text{eV}$ , indicating only a small contribution of charge transfer is present in the exciplex. The use of tetramethyl-1,2-dioxetane as a source of acetone triplets is described. Rate constants for quenching of acetone phosphorescence obtained using the dioxetane are in good agreement with those found by direct photoexcitation of acetone. Kinetic evidence is presented that indicates that the interaction of an excited-state molecule with tetramethyldioxetane leads to almost quantitative production of acetone triplets.

Elucidation of the mechanism of bimolecular luminescence quenching has been the object of much recent study. Regarding the photochemistry of carbonyl compounds, attention has centered on the mechanism of the Paterno-Buchi reaction,<sup>1</sup> the photocyclization of ketones to olefins yielding oxetanes. It has been shown that the reactive state in these cycloadditions is generally a carbonyl  $n, \pi^*$  excited state<sup>2,3</sup> and, based on the expected radical-like character of the oxygen in such a species,<sup>4</sup> the initial step in many of these reactions was long considered to be direct bond formation leading to an intermediate biradical (eq 1).<sup>1,2,5,6</sup>



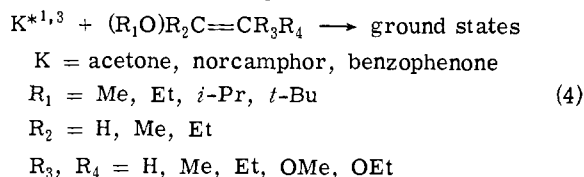
In the past decade, however, much evidence has been presented supporting the contention that the initial interaction between an excited-state molecule and a ground-state molecule is often formation of an excited molecular complex, or exciplex.<sup>7,8</sup> In a large number of cases (generally involving an aromatic component), emission of light has been detected from exciplexes in nonpolar solvents,<sup>8a,d,9</sup> and radical cations and anions have been observed in polar solvent systems.<sup>8d,9b,10</sup> These measurements have enabled characterization of these complexes with regard to lifetime, stability, and relationship to ground state (e.g., charge transfer) complexes (eq 2, 3).



In cases where the exciplex does not emit and does not dissociate into detectable ions, its presence has been inferred from a variety of indirect data. Several groups have studied the photocycloaddition of olefins to aromatic systems and have proposed the intermediacy of excited complexes in these reactions.<sup>8e-i</sup> Elegant studies of isotope effects<sup>8j-n</sup> and solvent effects (vide infra) on the photochemis-

try of aryl ketones have provided further insight into the nature of these so-called "invisible" exciplexes. Quantitative relationships between absolute fluorescence-quenching rate constants and quencher ionization potentials have been used to support the contention that charge-transfer interactions play a significant role in the formation and stability of these exciplexes.<sup>7-11</sup> Postulating a charge transfer-stabilized exciplex in the interaction between excited alkanones and electron-rich olefins is attractive in light of several recent studies.<sup>11h,j,12</sup>

We report here the fluorescence and phosphorescence quenching of several ketones with a series of electron-rich ethylenes (eq 4), and we compare this with ionization and



charge-transfer data on the olefins. The use of tetramethyl-1,2-dioxetane as a triplet acetone source and the kinetic data available therefrom are also presented with regard to the phosphorescence-quenching process.

## Results

**Quenching of Alkanone Fluorescence by Enol Ethers.** Addition of enol ethers to acetonitrile solutions of acetone or norcamphor results in a reduction of the alkanone fluorescence. Stern-Volmer analysis of the quenching was carried out using eq 5. The absolute fluorescence quenching rate

$$F^0/F = 1 + k_q \tau_F [Q] \quad (5)$$

constants,  $k_q$ , were determined from the slopes of the Stern-Volmer plots and the measured<sup>13</sup> singlet lifetimes,  $\tau_F$ , of acetone ( $1.7 \times 10^{-9}$  sec) and of norcamphor ( $5.7 \times 10^{-9}$  sec). The  $k_q$  values obtained vary over some two orders of magnitude for 15 olefins, with ethyl vinyl ether being the poorest quencher used and *cis*-1,2-diethoxyethylene and *cis*-1,2-dimethoxyethylene the best, with rates of quenching within an order of magnitude of diffusion controlled (Table I).

**Quenching of Ketone Phosphorescence by Enol Ethers.** Degassed solutions of benzophenone in Freon emit a readily observable phosphorescence at room temperature,<sup>14</sup> and this emission is quenched by the addition of enol ethers. Quenching rate constants have been determined both by

Table I. Quenching of Ketone Fluorescence by Enol Ethers<sup>a</sup>

Olefin	Number	Norcamphor $k_q \times 10^{-9}, M^{-1} \text{sec}^{-1}$	Acetone $k_q \times 10^{-9}, M^{-1} \text{sec}^{-1}$
	1	0.006	0.025
	2	0.018	0.05
	3	0.031	0.08
	4		0.22
	5	0.054	
	6		0.34
	7	0.14	0.32
	8	0.13	
	9	0.43	0.77
	10	0.44	0.70
	11	0.55	1.4
	12	0.72	
	13	0.80	1.8
	14	1.35	3.1
	15	1.44	2.9

<sup>a</sup> Aerated solutions of 0.1–0.4 *M* ketone in acetonitrile; error limits  $\pm 10\%$ .

monitoring of phosphorescence intensity and phosphorescence lifetime<sup>15</sup> as a function of olefin concentration. In the case of lifetime quenching, the Stern–Volmer expression takes the form of eq 6.

$$1/\tau_p = 1/\tau_p^0 + k_q[Q] \quad (6)$$

It has recently been observed in these laboratories<sup>16</sup> that deaerated solutions of acetone in acetonitrile emit a weak but detectable phosphorescence at room temperature. Although the phosphorescence is strongly masked by the acetone fluorescence in static measurements, use of the time-resolution capabilities of the single photon-counting technique makes measurement of phosphorescence lifetimes possible. We have determined acetone phosphorescence-quenching rate constants for several olefins by this technique, and these, together with the data for benzophenone quenching, are listed in Table II. The values reported here for acetone phosphorescence quenching were obtained at 46° to facilitate comparison with dioxetane decomposition experiments (vide infra) since  $\tau_p$  for acetone is temperature dependent.<sup>17</sup> By nitrogen bubbling acetonitrile solutions of acetone, we obtain  $\tau_p = 11 \mu\text{sec}$  at 46°, monitoring emission at 460 nm (cf.  $\lambda_{\text{max}}$  acetone fluorescence 405 nm).

**Ionization Potentials and Charge-Transfer Spectra of Enol Ethers.** In order to quantify the electron-donating ability of the olefins used in this study, three approaches were considered: theoretical calculation, measurement of vapor-phase ionization potentials, and measurement of solution charge-transfer spectra.

We utilized a simple Hückel MO method<sup>18,19</sup> to calcu-

Table II. Quenching of Ketone Phosphorescence by Enol Ethers

Olefin	Benzophenone <sup>a</sup> $k_q \times 10^{-9}, M^{-1} \text{sec}^{-1}$	Acetone <sup>b</sup> $k_q \times 10^{-9}, M^{-1} \text{sec}^{-1}$
1	0.08	0.020
2	0.14	
3	0.26	
7		0.094
10	1.1	0.34
13		0.64
15	4.1	1.25

<sup>a</sup> Solutions of  $10^{-3} M$  benzophenone in Freon, degassed by repeated freeze–pump–thaw cycles. Error limits  $\pm 20\%$ . <sup>b</sup> Solutions of 0.3 *M* acetone in acetonitrile, deaerated by nitrogen bubbling for 120 sec. Temp 46°. Error limits  $\pm 15\%$ .

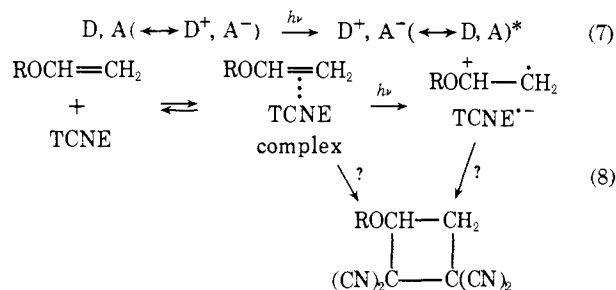
Table III. Comparison of  $k_q$  Values with Calculated  $E_{\text{HOO}}$ 's

Olefin type	$E_{\text{HOO}}$	Norcamphor $k_q \times 10^{-9}, M^{-1} \text{sec}^{-1}$
$\text{CH}_2=\text{CH}-\text{OR}$	$\alpha + 0.73\beta$	0.006 (R = OEt)
$\text{CH}_2=\text{C}(\text{CH}_3)\text{OR}$	$\alpha + 0.63\beta$	0.054
$\text{CH}_3-\text{CH}=\text{CH}-\text{OR}$	$\alpha + 0.56\beta$	0.13
$(\text{CH}_3)_2\text{C}=\text{CH}-\text{OR}$	$\alpha + 0.43\beta$	0.44

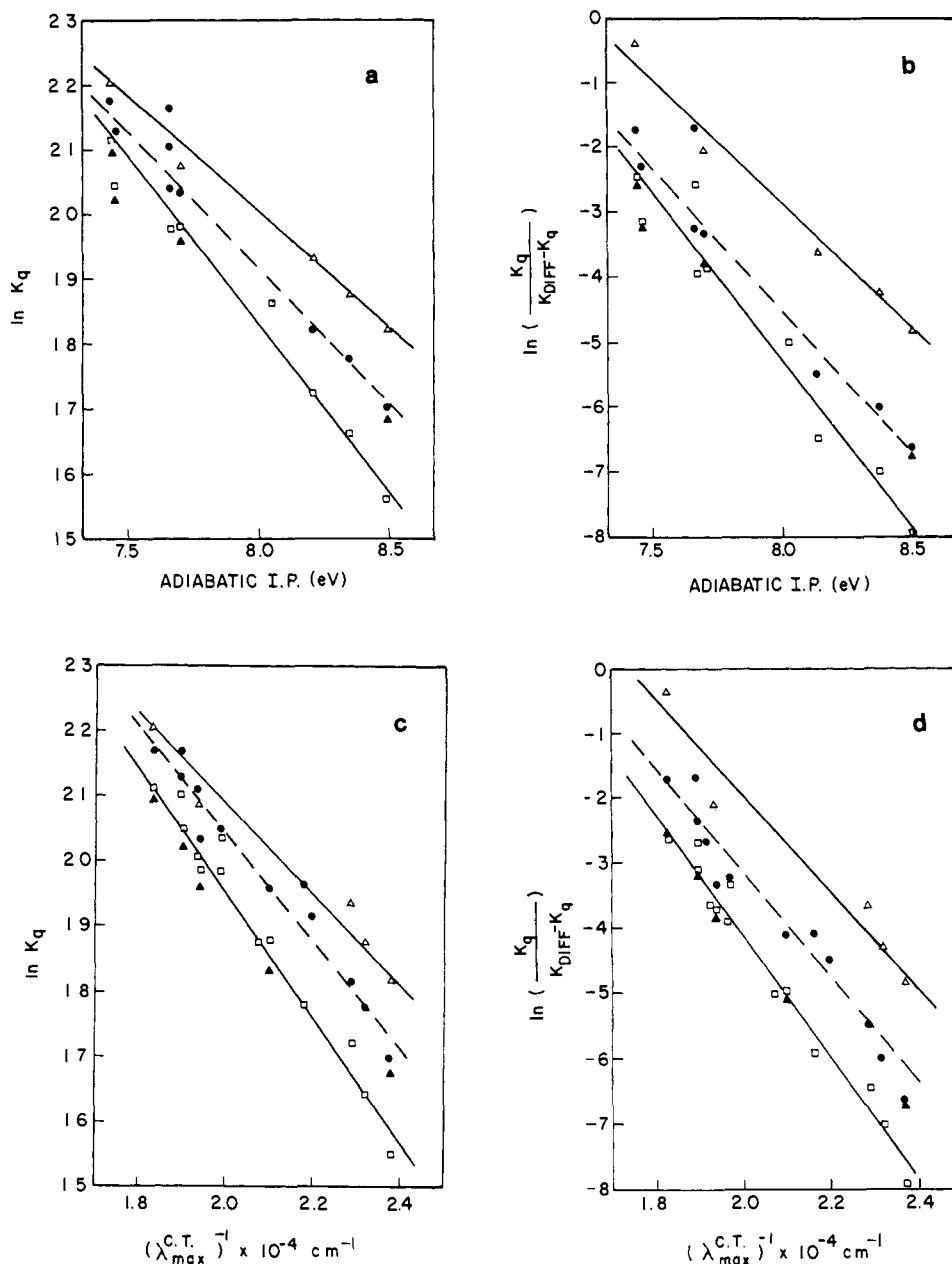
late highest occupied orbital (HOO) energies for several types of enol ethers in order to compare them with  $k_q$  values reported herein. Although this type of correlation is of a highly qualitative nature, it is clear (Table III) that increasing  $k_q$  values do correlate with increasing HOO energies within a series of monoalkoxyolefins.

The recent appearance of a report<sup>20</sup> describing the measurement of charge-transfer spectra between enol ethers and tetracyanoethylene (TCNE) prompted us to apply this technique to our series of quenchers. Mixing of cyclohexane solutions of any of the quenchers in Table I with dilute solutions of TCNE in methylene chloride yields intensely colored solutions ranging from yellow for 1 to purple for 15. The colors fade at different speeds for different olefins; e.g., at room temperature, the yellow color for 1 lasts for days, while the orange color from 3 lasts for only seconds. Following the latter process by NMR clearly showed the formation of 1,1,2,2-tetracyano-3-*tert*-butoxycyclobutane as the color faded, in accordance with literature reports on such systems.<sup>20,21</sup> Rapid scanning of these colored solutions provides uv–visible absorption data on these complexes. In all cases, these complexes show a single, broad, unstructured absorption band, presumably corresponding to the transition from a ground-state complex with relatively little charge separation (“no-bond structure”) to an excited state possessing substantial charge-transfer character (eq 7, 8).<sup>20,22</sup> The  $\lambda_{\text{max}}$  values for these complexes are given in Table IV along with gas-phase ionization potentials obtained by photoelectron spectroscopy.

**Correlations between Quenching and Ionization or Charge-Transfer Data.** Data treatment in such systems has



been discussed in detail by Evans<sup>11</sup> and Weller,<sup>8d</sup> and generally involves correlation of some log function of  $k_q$  with some function of ionization potential in order to implicate a charge-transfer quenching mechanism. Figure 1 shows four



**Figure 1.** Correlations between rate constants for luminescence-quenching and electron-donating parameters for enol esters. Symbols used: open triangles (upper solid line), benzophenone phosphorescence; filled circles (dotted line), acetone fluorescence; open squares (lower solid line), norcamphor fluorescence; filled triangles, acetone phosphorescence.

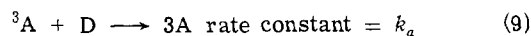
such correlations with our data, showing both the simple  $\ln k_q$  as well as the diffusion-rate corrected<sup>11i</sup>  $\ln [k_q / (k_{diff} - k_q)]$  function plotted against both adiabatic ionization potential<sup>9d</sup> and energy of the TCNE charge-transfer band of the respective quencher. In Figures 1b and 1d,  $k_{diff}$  for acetonitrile is taken to be  $2 \times 10^{10} \text{ sec}^{-1}$ , and for Freon,  $1 \times 10^{10} \text{ sec}^{-1}$ , based on the Debye equation.<sup>23</sup>

Despite the scatter in the data, it is reasonably clear that the data for all four excited states involved here (norcamphor and acetone singlets, benzophenone and acetone triplets) fall on lines with very similar slopes, indicating that all four ketonic  $n, \pi^*$  states show similar sensitivities to ionization potential or charge-transfer energy differences. Analogous results have been obtained for  $\alpha$ -diketones in these laboratories.<sup>24</sup>

**Quenching of Thermally Generated Acetone Triplets by Enol Ethers.** Thermal decomposition of tetramethyl-1,2-dioxetane (D) is an efficient way to generate acetone triplets in solution.<sup>25a</sup> In nitrogen-bubbled solutions of D in acetonitrile at 50°, the emission observed is >95% phospho-

rescence with a  $\lambda_{max} \sim 420 \text{ nm}$  (uncorrected). In addition, the net rate of depletion of D at this temperature is so small that ordinary static quenching experiments may be run assuming essentially constant [D] over the course of the experiment.<sup>25b</sup>

It is found, however, that the quenching constants,  $k_q \tau_p^{obsd}$ , obtained by ordinary Stern-Volmer analysis are dependent upon dioxetane concentration. In the case of quenchers with long triplet lifetimes, this dependence is quite large and is due primarily to sensitization of dioxetane decomposition by quencher triplets<sup>25c</sup> leading to regeneration of triplet acetone. In the case of the vinyl ethers, we find a less marked effect (Table V) which we ascribe to an inefficient but measurable quenching of triplet acetone by dioxetane (eq 9).



We have already shown<sup>25d</sup> that encounters between  ${}^3A$  and D retain electronic excitation with near unit efficiency (eq 10). Using the data from Table V with an equation de-

Table IV. Charge-Transfer Spectra and Ionization Potentials for Enol Ethers

Olefin	CT/TCNE <sup>a</sup>		Vertical IP, ev
	$\lambda_{\max}$ , nm	Adiabatic IP, ev	
1	422 <sup>b</sup>	8.49 ( $\pm 0.02$ )	9.07 ( $\pm 0.02$ )
2	431	8.36	8.89
3	437	8.19	8.75
4	455		
5	<i>c</i>		
6	464		
7	477		
8	484	8.04	8.53
9	509 <sup>b</sup>	7.65	8.20
10	516	7.70	8.20
11	517 <sup>b</sup>		
12	510		
13	526	7.40	8.23
14	526	7.63	8.39
15	543	7.38	8.15

<sup>a</sup>Spectra taken on Unicam SP-800A spectrometer; values  $\pm 3$  nm.

<sup>b</sup>Spectra taken on Cary 14 spectrometer; values  $\pm 1$  nm. <sup>c</sup>Complex too unstable to measure; estimated  $\lambda_{\max}$  462 nm.

Table V. Observed Quenching Constants for Thermally Generated Acetone Phosphorescence Quenched by *cis*- and *trans*-1,2-Diethoxyethylene<sup>a</sup>

[D], M	<i>cis</i> -DEE (15)	$k_q\tau_p^{\text{obsd}}, M^{-1}$	<i>trans</i> -DEE (13)
$5 \times 10^{-2}$	$2.5 \times 10^3$		$1.2 \times 10^3$
$3 \times 10^{-2}$	$4.3 \times 10^3$		$2.2 \times 10^3$
$1 \times 10^{-2}$	$7.4 \times 10^3$		$3.6 \times 10^3$
$6 \times 10^{-3}$	$9.6 \times 10^3$		$5.0 \times 10^3$
$2 \times 10^{-3}$	$1.22 \times 10^4$		$6.3 \times 10^3$
$2 \times 10^{-4}$	$1.45 \times 10^4$		$8.1 \times 10^3$
0 (extrapolated) <sup>b</sup>	$1.51 \times 10^4$		$8.5 \times 10^3$
	$1.37 \times 10^9$	$k_q^{\text{thermal}}, M^{-1} \text{sec}^{-1}$ <sup>c</sup>	$7.7 \times 10^8$
	$6.7 \times 10^{-2}$	$k_a/k_q^d$	$1.42 \times 10^{-2}$
	$0.9 \times 10^7$	$k_a, M^{-1} \text{sec}^{-1}$	$1.1 \times 10^7$

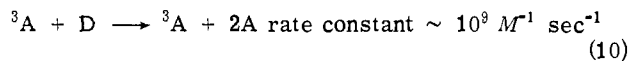
<sup>a</sup>Temp 48°; solutions deaerated by nitrogen bubbling for 120 sec.

<sup>b</sup>According to eq 11 (Figure 2). <sup>c</sup> $\tau_p$  measured by single-photon counting to be  $11 \pm 0.5 \mu\text{sec}$ ; error limits  $\pm 15\%$ . <sup>d</sup>Slopes derived from Figure 2.

Table VI. Parameters Obtained from Quenching of Dioxetane-Generated Acetone Triplets

Olefin	Photoexcited <sup>a</sup>		Thermal <sup>b</sup>	
	$k_q \times 10^9, M^{-1} \text{sec}^{-1}$	$k_q \times 10^9, M^{-1} \text{sec}^{-1}$	$k_q \times 10^9, M^{-1} \text{sec}^{-1}$	$k_q \times 10^9, M^{-1} \text{sec}^{-1}$
1	0.020		0.022	
7	0.094		0.117	
10	0.34		0.43	
13	0.64		0.77	
15	1.25		1.37	

<sup>a</sup>From Table II. <sup>b</sup>From extrapolation of data according to eq 11. Error limits  $\pm 15\%$ .



rived for competitive quenching (eq 11), we obtain directly

$$(k_q\tau_p^{\text{obsd}})^{-1} = (1 + k_a\tau_p[D])(k_q\tau_p^{\circ})^{-1} \quad (11)$$

$k_a \sim 10^7 M^{-1} \text{sec}^{-1}$  (Figure 2), thus confirming that the efficiency of the autocatalytic pathway (eq 10) with respect to the quenching pathway (eq 9) is roughly 99%.

Extrapolation of the quenching constants obtained in these experiments to zero [D] gives the  $k_q$  values listed in Table VI. The agreement between  $k_q$  values obtained by either photoexcitation and single-photon counting or by thermal dioxetane decomposition is quite good; the minor discrepancies observed may be of a systematic nature, e.g., an imprecision in measuring  $\tau_p$  values which would affect

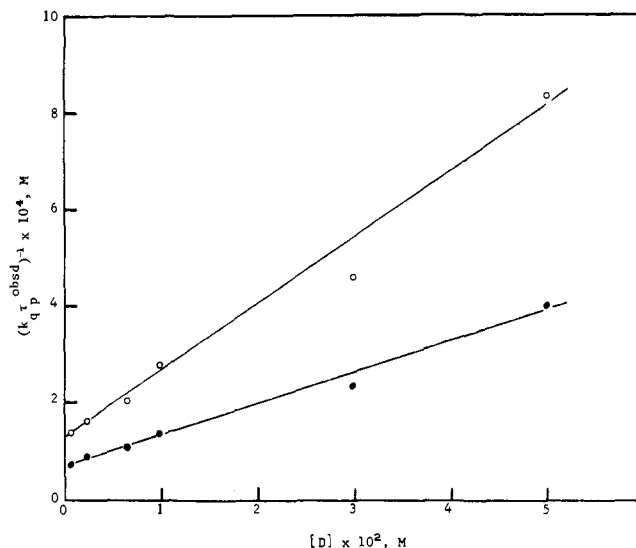


Figure 2. Dependence of  $k_q\tau_p^{\text{obsd}}$  on dioxetane concentration for *cis*- and *trans*-1,2-diethoxyethylenes (filled and open circles, respectively). Data plotted according to eq 11 (from Table V).

Table VII. Rates of Hydrolysis vs. Rates of Polymerization for Some Enol Ethers<sup>a</sup>

Olefin	$k_{\text{hydrolysis}}^{\text{rel}}$	$k_{\text{polymerization}}^{\text{rel}}$
	1.00	1.00
	0.12	1.64
	0.39	3.99
	<0.01	~5

<sup>a</sup>From ref 32.

$k_q^{\text{thermal}}$  (where an absolute  $\tau_p^{\circ}$  is required) differently from  $k_q^{\text{photoexcited}}$  (where ratios of  $\tau_p^{\circ}$  values were involved, eq 6).

## Discussion

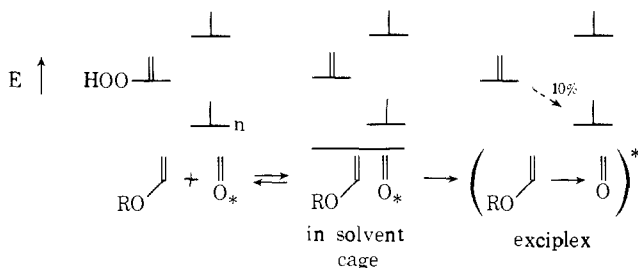
**Mechanism of Quenching Interaction.** In considering the nature of the interaction between enol ethers and  $n, \pi^*$  ketones, it is instructive to first examine the reactivity of enol ethers toward other electrophilic reagents. The structure-reactivity profiles for acid-catalyzed hydrolysis and cationic polymerization of enol ethers are strikingly different (Table VII).<sup>26</sup> In general, hydrolysis rates decrease as the olefin becomes more symmetrically substituted, while polymerization rates go up as substituents are added to the double bond.<sup>27</sup> On the bases of extended Hückel calculations, it was concluded that the hydrolysis reaction involves bonding of a proton to a specific carbon and reflects carbonium ion stabilities in its transition state, while polymerization involves delocalization of the entire  $\pi$  system of the ether toward an electrophilic center, and its rate reflects the stabilization due to this  $\pi$ -type complexation.

Our quenching data show a very similar structural dependence (Tables I and II) to the polymerization data, and we consider this evidence that the primary step in the quenching process is  $\pi$ -complex formation and not bond formation. The charge-transfer contribution to this excited  $\pi$  complex, or exciplex, may be estimated in several ways. Quenching processes which involve essentially complete electron transfer display linear  $\log k_q$  vs.  $\text{IP}_{\text{quencher}}$  with slopes approaching  $-17/\text{eV}$ ,<sup>28</sup> whereas processes involving only partial electron transfer show shallower slopes.<sup>9d, 11i-1, 29</sup> The slopes of the lines in Figure 1 (after

converting  $\ln k_q$  to  $\log k_q$ ) are roughly  $-1.5/\text{eV}$  to  $-2/\text{eV}$  indicating about "10–15% electron transfer"<sup>29</sup> or charge-transfer contribution is present in the complexes involved here. A second probe for extent of charge transfer is polar solvent effect. Whereas  $k_q(\text{CH}_3\text{CN})/k_q(\text{C}_6\text{H}_6) = 13$  for full charge transfer,<sup>7</sup> we have found<sup>19</sup> a negligible, or perhaps inverse, solvent effect,  $k_q(\text{CH}_3\text{CN})/k_q(\text{C}_6\text{H}_6) = 0.8 \pm 0.2$ . Small and inverse solvent effects have been observed in many systems believed to involve only fractional charge transfer in the quenching process.<sup>11,29,30</sup> It is significant that, in general we find that rates of phosphorescence quenching are smaller than those of fluorescence quenching. The causes of this are not at all clear but are consistent with our findings that maximum triplet quenching rates in fluid solution are significantly less than  $k_{\text{diff}}$ , while singlet-quenching processes have been found to proceed at the diffusion-controlled rate.

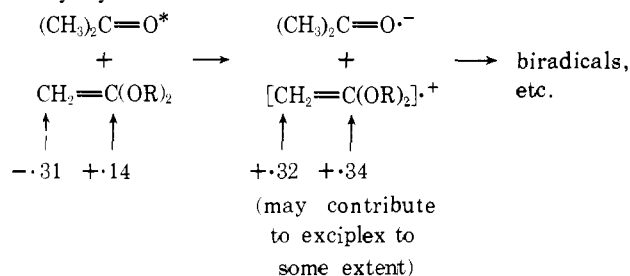
**Electronic Details of the Mechanism.** The singlet- and triplet-quenching processes may be considered in terms of simple orbital pictures. In both cases, partial charge donation from the olefin  $\pi$  orbital to the ketone  $n$  orbital produces the initial exciplex (Scheme I). Back-donation of

Scheme I



charge may then occur directly in the singlet exciplex to yield ground states, while the triplet exciplex must first intersystem-cross to the singlet. Finally, both singlet and triplet exciplexes are capable of bond formation leading to biradicals and, eventually, to oxetanes. This latter process has the advantage of predicting less regiospecific oxetane formation than pathways based on direct biradical formation.<sup>19</sup> As electron density is removed from HOO of an enol ether, simple MO calculations indicate that the charge densities at the two carbons become more equal (Scheme II).

**Scheme II.** Comparison of Charge Distribution at the Ethylenic Carbons for the Ground State and Radical Cation of a 1,1-Dialkoxyethylene



Thus charge transfer from the enol ether to the ketone in the exciplex tends to reduce the nucleophilicity difference between the carbons of the olefin, thereby reducing the selectivity in bond formation with the electrophilic ketone oxygen to yield a biradical.

### Summary

We have found that luminescence quenching of  $n\pi^*$  ketones by enol ethers proceeds via initial exciplex formation, which leads to deactivation either by bond formation yielding a biradical, or by a net catalytic internal conversion, formulated as a two-way electron transfer. The exciplex is

considered to possess a rather small amount of charge-transfer character, which, however, appears to play a significant role both in the decay of the exciplex to ground-state olefin and ketone as well as its collapse to a biradical.

### Experimental Section

**Reagents.** Acetone (Fisher Spectranalyzed) was used as received. Norcamphor (Aldrich) was sublimed three times at steam-bath temperature and aspirator pressure. Benzophenone (Columbia Organic) was recrystallized from ethanol and sublimed. Acetonitrile (Matheson Coleman Bell) was purified according to the procedure of O'Donnell et al.<sup>31</sup> Freon (1,1,2-trichlorotrifluoroethane; Matheson Coleman Bell) was purified by passing through a 12 in. column of activity 1 alumina (Woelm) and distilled. Cyclohexane (Fisher) was shaken with concentrated sulfuric acid, washed, dried, and distilled from calcium hydride. Methylene chloride (Amend) was distilled from calcium hydride. Tetracyanoethylene (City Chemical) was sublimed twice at steam-bath temperature (0.1 mmHg).

**Vinyl Ethers.** Ethyl vinyl ether (**1**) (Aldrich) was dried over potassium hydroxide and distilled. Isopropyl and *tert*-butyl vinyl ethers (**2** and **3**) were prepared from the respective alcohols<sup>32</sup> and purified by VPC collection (20 ft  $\times$  0.25 in. 20% Carbowax 20M on base-washed Chromosorb P, 100°) followed by distillation (method A). *cis*- and *trans*-1-methoxy-1-butenes (**6** and **7**) were supplied by Dr. P. Wriede<sup>5d</sup> and purified by method A, above. 1,4-Dioxene (**11**) (Aldrich) was purified by VPC collection (4.5 ft  $\times$  0.25 in. 20% Carbowax 20M and 1% KOH on base-washed Chromosorb P, 70°) followed by distillation (method B). The remaining olefins were prepared by Dr. M. Niemczyk according to the procedures cited and purified as described: methyl and ethyl isopropenyl ethers (**4** and **5**) from acetone dimethyl or diethyl ketal and phosphoric acid (method A);<sup>33</sup> *cis*-1-ethoxy-1-propene (**8**) from propionaldehyde diethyl acetal (method A);<sup>33</sup> methyl and ethyl 2-methylpropenyl ethers (**9** and **10**) from isobutyraldehyde dimethyl and diethyl acetals<sup>34</sup> (method A); *cis*-1,2-dimethoxy- and -diethoxyethylenes (**14** and **15**) from 1,1,2-trimethoxy- and -triethoxyethanes<sup>35</sup> (VPC on 10 ft  $\times$  0.25 in. 20% XF-1150 on base-washed Chromosorb P, 105°, followed by distillation, method C); and their respective *trans* isomers (**12** and **13**) by sensitized isomerization using xanthone for **12** and biacetyl<sup>36</sup> for **13** (method C).

**Tetramethyl-1,2-dioxetane (D)** was prepared using the general method of Kopecky and Mumford<sup>37</sup> modified by Dr. P. Lechtken and Dr. H.-C. Steinmetzer as follows. To a flask containing 50 ml of dry ether (Mallinckrodt) cooled to 0° with an acetone bath and some Dry Ice was added 9 ml of 98% hydrogen peroxide (FMC Corp.) [DANGEROUS EXPLOSIVE]<sup>38</sup> over a period of 2–3 min with stirring. The solution was cooled to  $-40^\circ$  by adding more Dry Ice to the bath, and 4.8 g of tetramethylethylene (Aldrich Gold Label) was added over a period of 2–3 min. Solid 1,3-dibromo-5,5-dimethylhydantoin (Matheson Coleman Bell) (8.1 g) was added in portions over 30 min at  $-40^\circ$  with efficient stirring. The mixture was allowed to stir for 2 hr at  $-40^\circ$  and 4 hr at room temperature. The solution was washed with  $5 \times 50$  ml of saturated, aqueous  $\text{K}_2\text{CO}_3$  (frothing!) and  $2 \times 50$  ml of water, dried over  $\text{Na}_2\text{CO}_3$ , and filtered. Rotary evaporation left a semisolid mass which was dissolved in a minimum amount of pentane at room temperature and precipitated by cooling to  $-78^\circ$ . Yield (two crops) was 7.6 g (68%) of 2-bromo-3-hydroperoxy-2,3-dimethylbutane, mp  $95\text{--}99^\circ$  ( $102\text{--}103^\circ$  after reprecipitation from pentane at  $-78^\circ$ ). The bromohydroperoxide was dissolved in 75 ml of ether at 0° (ice bath) and 7.5 g of silver acetate (Baker) added in portions with efficient stirring over 30 min in the dark. The solution was allowed to warm up slowly to room temperature and filtered. The solids were washed with  $5 \times 20$  ml of ether. The combined ethereal solutions were washed with 50 ml of ice-cold water,  $5 \times 50$  ml of ice-cold 10% aqueous NaOH, and 50 ml of ice-cold water, dried over  $\text{MgSO}_4$  for 1 hr at  $-10$  to  $-20^\circ$ , and filtered. Most of the solvent was rotary evaporated at room temperature, leaving a yellow liquid which solidified when cooled in ice. This material was dissolved in a minimum amount of pentane at  $30^\circ$  in Craig tubes, cooled to  $-78^\circ$ , and centrifuged to remove solvent (colorless). The yellow crystals were redissolved in pentane which was again cooled to  $-78^\circ$  and centrifuged. In this manner, 0.5 g (15%) of tetramethyl-1,2-dioxetane was isolated as sweet-smelling yellow nee-

dies, mp 77.5–79.0° (rapid heating to 65°). These were stored at –10 to –20°.

**Fluorescence Quenching.** Solutions of 0.1–0.4 *M* acetone or norcamphor in acetonitrile were prepared. Two identical 2-ml ketone solutions were prepared in 1-cm quartz cuvettes for each experiment. One solution was used as a standard, and its fluorescence intensity taken to reflect small fluctuations in the excitation source over the course of the experiment. The fluorescence intensity of the second solution was measured both in the absence of quencher and after the addition of aliquots of vinyl ether by syringe. Fluorescence was monitored at the  $\lambda_{\text{max}}$  of the emission using the Hitachi Perkin-Elmer MPF-2A spectrofluorimeter at room temperature. All samples were irradiated at 313 nm and  $F^\circ/F$  ratios established. All solutions were checked periodically on a Gilford uv spectrometer for competitive absorption by the vinyl ethers, and the  $F^\circ/F$  values corrected accordingly. In all cases, at least five determinations of fluorescence peak height were made for both sample and standard solutions to ensure good precision.

For vinyl ethers with low  $k_q$  values, individual solutions were made up for each concentration of quencher. The procedure thereafter was identical.

**Phosphorescence Quenching of Benzophenone.** Solutions of 1.0–1.5  $\times 10^{-3}$  *M* benzophenone in Freon were prepared with and without measured amounts of quenchers. These were degassed on a vacuum line using generally 9–11 freeze-pump-thaw cycles. The final pressure above the frozen solution before sealing off the sample was generally less than 2  $\mu\text{m}$ . Stern–Volmer quenching data were obtained at room temperature both by monitoring phosphorescence peak height at 450 nm using the Hitachi Perkin-Elmer MPF-2A spectrofluorimeter, and by measuring the phosphorescence lifetime directly on a Xenon Corp. Noratron-789A nanopulser<sup>15</sup> ( $\tau_p \sim 100$   $\mu\text{sec}$  generally). Agreement between the two methods was  $\pm 20\%$  or better.

**Phosphorescence Quenching of Photoexcited Acetone.** Solutions of 0.3 *M* acetone in acetonitrile were prepared with or without measured amounts of quencher in quartz cuvettes fitted with Teflon stopcocks. These solutions were cooled to –35 to –40° and bubbled with nitrogen (Airco) for 120 sec using a glass capillary. The deaerated solutions were placed into a thermostated cell holder, kept at 46° by a Lauda K4R constant-temperature bath, in the single-photon counting apparatus. Phosphorescence lifetimes were determined by collecting data for approximately 1 hr per sample, using a lamp (air-spark) flash rate of 10 kHz, time-to-amplitude converter range of 10  $\mu\text{sec}$ , and a pulse-height analyzer calibrated at 31.1  $\mu\text{sec}$  per channel. Under these conditions,  $\tau_p$  was  $\sim 11$   $\mu\text{sec}$  for acetone in the absence of quencher. With the photomultiplier cooled to –78° with Dry Ice, thermal noise was kept to a minimum (ca. 10 counts per channel). Subtraction of noise counts from total signal (up to several hundred counts per channel) gave good phosphorescence decay data.

**Quenching of Thermally Generated Acetone Phosphorescence.** Solutions of varying concentrations of tetramethyl-1,2-dioxetane (e.g., see Table V) in acetonitrile with or without measured amounts of quencher were prepared and nitrogen-bubbled in the same manner as the acetone solutions described above. These were preheated in the Lauda K4R water bath at 48° and placed in the thermostated cell holder of the MPF-2A. The chemiluminescence intensity at 420 nm (>95% acetone phosphorescence) was allowed to maximize (2–3 min), and the values obtained were analyzed according to a modified Stern–Volmer treatment as described. It was found that the intensity of emission remained essentially constant at its maximum value for several minutes at 48°, reflecting the relatively slow decomposition of the dioxetane under these conditions.

**Measurement of Charge-Transfer Spectra.** Solutions of approximately 1 *M* enol ether in 1.8 ml of cyclohexane were placed in quartz cells in the cell holder of a Unicam SP-800A absorption spectrometer. Then 0.2 ml of a solution of 1.3  $\times 10^{-2}$  *M* tetracyanoethylene in methylene chloride was added rapidly and the spectral region from 400 to 600 nm manually scanned very rapidly in both directions (i.e., toward increasing and decreasing  $\lambda$ ) several times. The average of the  $\lambda_{\text{max}}$  values obtained for an equal number of scans in each direction was taken to be the  $\lambda_{\text{max}}$  of the complex. Calibration of the technique was achieved by running spectra of the relatively long-lived TCNE complexes of **1**, **6**, **9**, and **11** on a Cary 14 absorption spectrometer.

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## Novel Fluorescent Probe for Micellar Systems. 1,3-Dialkylindoles

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**Abstract:** The fluorescent properties of several 1,3-dialkylindoles are described in terms of their potential value as fluorescent probes for micellar systems. These compounds display shifts in fluorescence  $\lambda_{\max}$  from 370 to 350 nm and in fluorescence lifetime from 19 to 8 nsec in going from aqueous to micellar environment. One such compound, 11-(3-hexyl-1-indolyl)undecyltrimethylammonium bromide (**5**), forms micelles at concentrations above  $10^{-4}$  M and is readily incorporated into micelles of other cationic surfactants. This indole is useful in determining the critical micelle concentrations (cmc's) of cationic surfactants because of the large shift in its fluorescence spectral distribution upon incorporation into a host surfactant micelle. In addition, use of a wavelength-correlated single photon-counting technique allows resolution of the fluorescence of this compound into aqueous and micellar components in the vicinity of its cmc.

The nature of the intramicellar environment has been the subject of extensive study for decades.<sup>1</sup> Over the years, a simple schematic description of the micelle has evolved based predominantly on measurements of macroscopic solution properties and effects of micelles on chemical reactions.<sup>1</sup> Figure 1 illustrates the typical spherical micelle that is formed in aqueous solutions of roughly  $10^{-3}$  to  $10^{-2}$  M ionic surfactant. The micelle consists of a liquid hydrocarbon-like core surrounded by a highly charged layer (Stern layer) containing ionic head groups of the individual surfactant molecules, oppositely charged counterions, and water. The simplicity of this model raises a number of questions concerning its applicability in detail. For example, how hydrocarbon-like is the micellar core, with respect to polarity (i.e., presence or absence of water), viscosity, or air solubility? Micelles are in dynamic equilibrium with monomeric (i.e., unassociated) surfactant molecules in solution; individual micelles are thought<sup>1</sup> to remain intact no longer than  $10^{-4}$  sec. Thus techniques used to probe the micelle must operate on short enough time scales to provide essentially instantaneous rather than time-averaged information. Measurements of processes such as fluorescence, operating over very short (e.g., nanosecond) time periods, appear to be uniquely adaptable to studies of this nature.

Fluorescent probes have long been employed to provide information on the microenvironments of biological macromolecules and larger structures including membrane systems.<sup>2</sup> More recently, the use of fluorescent probes in surfactant systems has become popular as interest in the nature of the micellar interior grows.<sup>3</sup> In earlier studies, ionic or zwitterionic aromatic molecules were commonly employed due to the extreme sensitivity of their fluorescent

yields to solvent polarity. Recently, however, objections have been raised concerning the validity of using highly polar probes for hydrophobic regions such as micellar interiors,<sup>4,5</sup> and most recent studies<sup>3,5</sup> have utilized aromatic hydrocarbons as probes that would be less likely to perturb the properties of the host system under investigation.

The versatility of the fluorescence technique is illustrated in the varied nature of these studies. Included among the types of measurements involved are excitation and emission spectra,<sup>6</sup> emission decay rates<sup>7</sup> and quantum yields,<sup>8</sup> and static as well as dynamic fluorescence polarization.<sup>9</sup> Fluorescence spectra and polarization experiments<sup>3e,1</sup> support the general contention that the core of the micelle is liquid hydrocarbon-like with respect to polarity and viscosity, but other studies based on quantum yields of excimer fluorescence indicate a very high (or perhaps anisotropic) viscosity in the micellar interior.<sup>3c,g</sup> Fluorescence lifetime and quenching measurements<sup>3b,f,5</sup> have provided information concerning the general location of solubilized fluorescent molecules in the micelle and their accessibility to quenchers located either in the bulk aqueous medium or deep inside the micelle. With regard to these studies, the question of oxygen solubility in micelles has arisen;<sup>3c,5</sup> as yet, no clear-cut answer has been forthcoming on this point.

We report here an extension of earlier studies made in these laboratories<sup>5</sup> using fluorescence-decay techniques<sup>10,11</sup> to analyze the behavior of small fluorescent molecules in solutions of micelle-forming surfactants. We have evaluated a series of 1,3-dialkylindoles as potentially versatile and powerful fluorescent probes for micelle structure, amenable to both static and dynamic, including time-resolved, fluorescence spectral measurements.