where

$$V_{\mathrm{atom}}(A) \equiv \left\langle 0 \middle| \sum_{i}\sum_{i' \neq i} r_{ii'}{}^{-1} \middle| 0 \right\rangle - 2\langle 0|r_{Ai}{}^{1}-|0\rangle \qquad (22)$$

The first term in eq 2 is just the potential energy arising from the dipole–dipole interaction of the atom dipoles. If the free atom terms do not change with respect to internal rotation and kinetic energy effects are neglected, we should be able to evaluate the barrier to internal rotation by calculating the change in the dipole–dipole interaction using the parameters in GTF for the atom dipoles. For ethane we found the dipole–dipole contribution to be $\Delta V_{\mathrm{dip}} = 392$ cal/mol compared to the experimental barrier of 2928 ± 25 cal/mol.[14] This result indicates that barriers to internal rotation may arise from subtle changes in V_{atom}.[15] The magnitude of these changes can be estimated in ethane where $e^2 \cdot V_{\mathrm{atom}}(\mathrm{H}) = (4mc^2/e^2N)\sigma_{\mathrm{av}}{}^{\mathrm{d}}(\mathrm{H})$. We found that a 0.07% change in $V_{\mathrm{atom}}(\mathrm{H})$ would account for the observed barrier. Subtle changes in the calculated electron distribution of ethane have been noted by Jorgensen and Allen.[16]

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged.

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Physical Evidence for Complex Formation between Olefins and *trans*-Glyoxal ^3A_u

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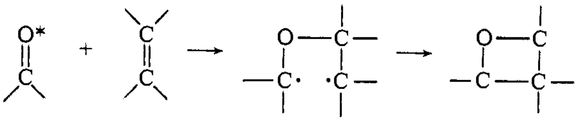
Abstract: The gas-phase quenching of *trans*-glyoxal ^3A_u (lowest energy n,π* triplet state) by the olefins ethylene, butene-1, and isobutylene at 300°K has been examined by a time-resolved phosphorescence technique using tunable dye laser excitation. Significant deviations from Stern–Volmer quenching behavior are observed. The results may be explained by assuming that a collision complex is reversibly formed during olefin–glyoxal ^3A_u collisions. A number of rate constants concerning the formation and subsequent reactions of the complex may be derived. The nature of the collision complex is discussed in terms of current observations on the photochemistry of n,π* triplet states.

The triplet n,π* excited electronic states of carbonyl-containing compounds undergo a large number of important photochemical and photophysical processes.[2a] The rich photochemistry of these molecules is presumably a reflection of (1) the relatively long (~milliseconds) lifetimes of n,π* triplets and (2) the nucleophilic and electrophilic behavior of the C atom and O atom, respectively, or the radical-like behavior of n,π* electronic configurations. Of particular interest has been the photochemical reaction of n,π* triplets with olefins to produce oxetanes when electronic energy transfer to the olefin is energetically unfavorable.[2b] Stereochemical studies have suggested that oxetane formation is preceded by biradical formation.[3]



Recently Kochevar and Wagner[4] have presented chemical evidence that the biradical formation itself may be preceded by the rate-limiting formation of a charge-transfer complex. In this paper we report physical evidence for the formation of a relatively stable collision complex between *trans*-glyoxal ^3A_u (n,π* triplet) and several olefins. It is possible that this collision complex is either the charge-transfer complex or the biradical.

There is a considerable amount of photophysical and photochemical information available concerning glyoxal (HCOCOH). Spectroscopic studies have shown the presence of two low-lying electronic states of *trans*-glyoxal: a ^1A_u (n,π*) state lying 21,978 cm^{-1} above the ^1A_g ground state and a ^3A_u (n,π*) state 19,198 cm^{-1} above the ground state.[5] Although theory predicts additional singlet and triplet B_g states in the same energy region,[6] recent calculations[7] supported by photoelectron spectroscopy[8] indicate that these states may be much higher in energy than the A_u states. Glyoxal may also exist in the cis form. The $^1B_1$ excited state of the cis form lies 350 cm^{-1} *below* the ^1A_u state of the trans form.[9] However, this state does not correlate with the ^1A_u and may thus be thought of as a separate molecular species. Also, the $^3B_1$ state of *cis*-glyoxal is

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[1] Alfred P. Sloan Foundation Fellow.

[2] (a) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968); (b) D. R. Arnold, R. L. Hinman, and A. H. Blick, *Tetrahedron Lett.*, 1425 (1964).

[3] See, for instance, J. Saltiel, K. R. Neubergen, and M. Wrighton, *J. Amer. Chem. Soc.*, **91**, 3658 (1969), or N. J. Turro and P. A. Wriede, *ibid.*, **92**, 320 (1970).

[4] I. H. Kochevar and P. J. Wagner, *ibid.*, **92**, 5742 (1970).

[5] (a) W. Goetz, A. J. McHugh, and D. A. Ramsay, *Can. J. Phys.*, **48**, 1 (1970); (b) J. Paldus and D. A. Ramsay, *ibid.*, **45**, 1389 (1967).

[6] (a) H. L. McMurry, *J. Chem. Phys.*, **9**, 231 (1941); (b) *ibid.*, **9**, 241 (1941).

[7] J. R. Swenson and R. Hoffman, *Helv. Chim. Acta*, **53**, 2331 (1970).

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[9] G. N. Currie and D. A. Ramsay, *Can. J. Phys.*, **49**, 317 (1971).

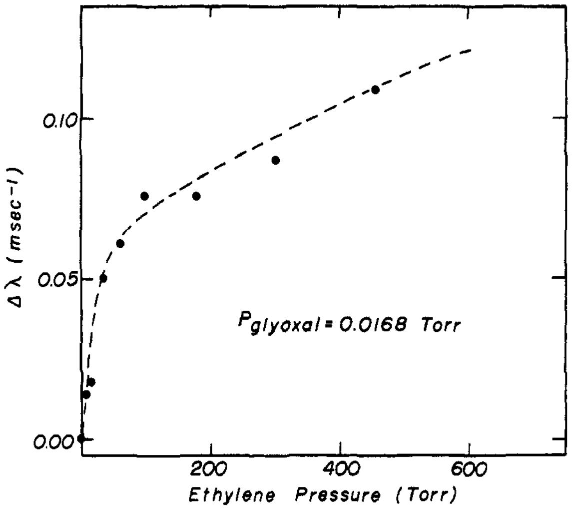

Figure 1. Stern–Volmer plot for addition of ethylene to glyoxal ^3A_u.

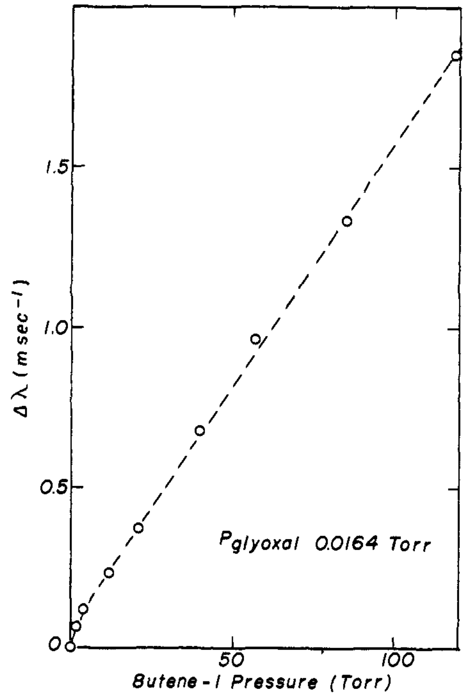

Figure 2. Stern–Volmer plot for addition of butene-1 to glyoxal ^3A_u.

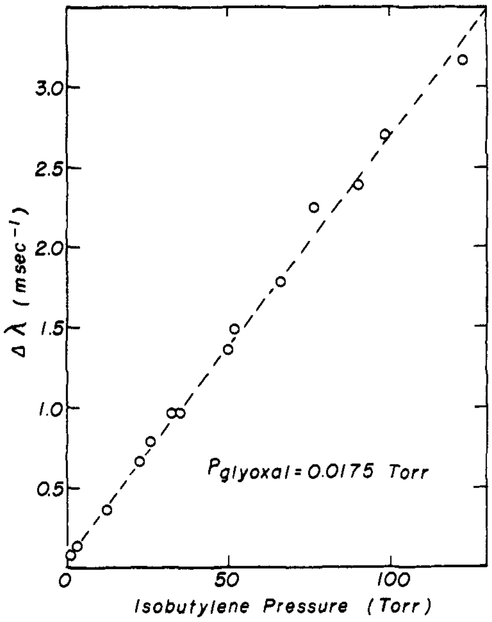

Figure 3. Stern–Volmer plot for addition of isobutylene to glyoxal ^3A_u.

expected to lie in the same energy region, with $^1A_2$ and $^3A_2$ states somewhat higher in energy.[7]

Upon excitation into the 0–0 band of the ^1A_u state at pure glyoxal pressures in the micron range fluorescence may be observed.[10,11] The decay of the ^1A_u state at zero pressure apparently is primarily radiative with an observed lifetime of 2.16 μsec. The addition of collision partners results in very efficient quenching of the ^1A_u fluorescence[11] (cross sections ~2–20 Å^2). This quenching is accompanied by the appearance of long-lived (milliseconds) emission which may be attributed to the ^3A_u state.[12] A study of quenching of the ^3A_u state by *trans*-glyoxal ^1A_g, coupled with photochemical data, has suggested the existence of a collision complex from which elimination of CO may take place.[12] Relatively efficient quenching by O_2 and NO may also be chemical in nature.[12] The collision-free lifetime of vibrationally relaxed glyoxal ^3A_u is 3.3 msec.[12]

Experimental Section

Since the experimental apparatus has been described in detail elsewhere,[11,12] only a brief account will be given here. A short pulse (~5 nsec) of intense (~1 kW) radiation from a N_2-laser-pumped dye laser is tuned to the 0,0 band of the $^1A_u \leftarrow {}^1A_g$ glyoxal absorption. The laser beam is directed to a 10-cm diameter cell containing a very low pressure of glyoxal and a measured amount of additive. Luminescence from excited glyoxal molecules is observed with an EMI 9558 QA phototube fitted with a 5000-Å long-pass filter. The short-lived (<2 μsec) fluorescence is removed electronically, and the time behavior of the longer lived (~ milliseconds) phosphorescence is recorded digitally with a transient recorder (Biomation, Model 610). Paper tapes containing the intensity-time behavior are analyzed by computer. Careful examination of the phosphorescence decay shows no evidence of nonexponentiality in the experiments reported here within the 6-bit accuracy of the transient recorder. Lifetimes are determined with a typical reproducibility of better than 2%. The glyoxal is carefully purified by repeated high-vacuum distillations. Ethylene, butene-1, and isobutylene are Phillips Research Grade. Gas pressures are measured with a calibrated pressure transducer for pressures below 5 Torr and with a mercury manometer for higher pressures. For additive pressures above 1 Torr, it has been shown that wall collisions do not contribute to triplet quenching.[10] The experiments are carried out at room temperature (300°K).

Results

A. General Observations. Figures 1, 2, and 3 show plots of Δλ, the inverse of the observed glyoxal ^3A_u lifetime in the presence of additive less the inverse of the lifetime for no additive, against pressure for the additives ethylene, butene-1, and isobutylene. Each point on the graphs represents an average of four to eight individual experiments. The glyoxal pressure is approximately 0.017 Torr for each experiment. Several striking features are evident. (1) In each case Δλ is *not* directly proportional to additive pressure, indi-

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(10) C. S. Parmenter and H. M. Poland, *J. Chem. Phys.*, **51**, 1551 (1969).

(11) J. T. Yardley, G. W. Holleman, and J. I. Steinfeld, *Chem. Phys. Lett.*, **10**, 266 (1971).

(12) J. T. Yardley, *J. Chem. Phys.*, **56**, 6192 (1972).

cating that a Stern–Volmer quenching mechanism[13] (*i.e.*, simple collisional quenching of the ^3A_u state) will not explain the observations. This effect is most pronounced for ethylene. For isobutylene, the curve appears linear in the pressure region studied, but does not pass through the origin. Unfortunately it is not possible to use additive pressures below about 1 Torr because of the effects of wall collisions.[12] (2) The initial slopes of the curves from the origin are in the order isobutylene > butene-1 > ethylene. (3) The transition to nonlinearity occurs at increasingly lower pressures in going from ethylene to butene-1 to isobutylene.

Since a simple Stern–Volmer quenching mechanism *will not* explain the observed behavior, possibilities for deviations from Stern–Volmer behavior must be examined. Systematic effects, such as those introduced by observation geometry or wall collisions, may be ruled out since experiments with inert additives such as Ar show no such behavior.[12] They may also be ruled out on theoretical grounds.[14] The pressures used are much too low for any of the quenching processes to become diffusion limited.[15] Deviations from Stern–Volmer behavior could occur as a result of incomplete vibrational relaxation of the glyoxal ^3A_u. However such effects would be expected to be more pronounced for inert additives such as Ar than for polyatomics such as ethylene, which should be efficient vibrational relaxers. The existence of several energetically accessible electronic states of *trans-* and *cis-*glyoxal and the possibility of a photochemical intermediate as a result of glyoxal ^3A_u-additive collisions suggest that the observed behavior may result from the inclusion of one or more intermediate states in the decay kinetics. A relatively simple kinetic model for such a situation is given in the next section.

B. Kinetic Model. In this section a kinetic model is proposed which will produce the behavior shown in Figures 1–3. The model is similar to one used to describe the kinetics of exciplex formation in aromatic compounds[16] and is conceptually the same as one used to describe vibrational energy transfer in several molecular systems.[17] In order to maintain simplicity, collisions involving ground-state glyoxal will not be considered, except where they contribute to the observed lifetime extrapolated to zero additive pressure. Also the kinetics of the singlet state will not be explicitly considered, since at the pressures under consideration intersystem crossing is effected in a very short time. Complete vibrational relaxation of the triplet state is assumed. In what follows, (^{3}G) and (E) will represent the partial pressures of glyoxal ^3A_u and of additive, and (H) will denote the partial pressure of some physical or chemical state available as a result of glyoxal ^3A_u-additive collisions. Such a state might be another low-lying electronic state of glyoxal or some sort of complex between glyoxal ^3A_u and the additive. The following kinetic processes may be considered.

(1)	$^3G \xrightarrow{k_0}$	quenching, radiation, photochemistry in absence of added gas
(2)	$^3G + E \xrightarrow{k_f}$	quenching and direct photochemistry not involving a possible equilibrium with an intermediate
(3)	$^3G + E \xrightarrow{k_h} H$	complex formation or physical conversion
(4)	$H \xrightarrow{k_h''} {}^3G + E$	unimolecular decomposition
(5)	$H + E \xrightarrow{k_h'} {}^3G + E$	collisional decomposition
(6)	$H \xrightarrow{k_t}$ product	unimolecular chemistry (and possibly radiation)
(7)	$H + E \xrightarrow{k_w}$ product	collisional chemistry

It should be noted that the rate constant k_0 contains collisional processes with ground state glyoxal molecules and thus is a constant only for constant glyoxal pressure.

The differential equations governing the time behavior of (^{3}G) and (H) are

$$(d/dt)(^3G) = -\alpha(^3G) + \beta(H)$$

$$(d/dt)(H) = \gamma(^3G) - \eta(H)$$

where $\alpha = k_0 + (k_f + k_h)(E)$, $\beta = k_h'' + k_h'(E)$, $\gamma = k_h(E)$, and $\eta = k_h'' + k_t + (k_h' + k_w)(E)$. Solution of the differential equations, subject to the initial condition that $(^3G)_{(t=0)} = N^0$ and $(H)_{(t=0)} = 0$, gives

$$(^3G)_{(t)} = N^0(\lambda_1 - \lambda_2)^{-1} \times [(\alpha - \lambda_2)\exp(-\lambda_1 t) + (\lambda_1 - \alpha)\exp(-\lambda_2 t)] \quad (1)$$

where the two decay constants are given by $\lambda_1\lambda_2 = \alpha\eta - \beta\gamma$ and $\lambda_1 + \lambda_2 = \alpha + \eta$. If $(\alpha - \eta)^2 > 4\beta\gamma$ (which is always the case at sufficiently low pressures or for certain rate constant combinations), then $(^3G) \cong N^0 \exp(-\lambda_1 t)$ and $\lambda_1 \cong \alpha - \beta\gamma(\eta - \alpha)^{-1}$ to first order. Under these conditions simple exponential behavior will be observed for (^{3}G). If we let $\Delta\lambda = (\tau^{-1})_{obsd} - (\tau^{-1})_{(E)=0}$, then $\Delta\lambda$ is of the form

$$\Delta\lambda \cong P(E) - [Q(E) + R(E)^2][S + T(E)]^{-1} \quad (2)$$

where $P = k_f + k_h$, $Q = k_h k_h''$, $R = k_h k_h'$, $S = k_h'' + k_t - k_0$, and $T = k_h' + k_w - k_f - k_h$.

C. Experimental Determination of Rate Constants. Comparison of the observed behavior of $\Delta\lambda$ as a function of added ethylene pressure (Figure 1) with eq 2 above allows some important conclusions to be drawn concerning the rate constants. The term S must be significant at the pressures employed; otherwise $\Delta\lambda$ would be linear in (E). Similarly T must be significant since neglect of T would give $[\Delta\lambda/(E)]$ linear in (E) which is also not observed. The relative importance of Q and R may be examined in the following way. The constant P may be estimated from the intercept of a graph showing $[\Delta\lambda/(E)]$ *vs.* (E). Although the uncertainty in extrapolation is large due to the curvature of the plot and the lack of data at low pressures (where wall collisions may interfere), the intercept may be found to be $P = (49 \pm 4) \times 10^{-4}$ msec^{-1} Torr^{-1}. Equation 2 may be rewritten

$$\{P - [\Delta\lambda/(E)]\}^{-1} = [S + T(E)][Q + R(E)]^{-1} \quad (2')$$

Now, if R is negligible over the pressure range used in

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(13) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 663.

(14) P. B. Sackett and J. T. Yardley, *J. Chem. Phys.*, **57**, 152 (1972). It should be noted that, at pressures employed here, the mean free path is less than the cell dimension. Thus the time to reach the walls is diffusional in nature. See ref 12.

(15) W. D. Gardiner, Jr., "Rates and Mechanisms of Chemical Reactions," W. A. Benjamin, New York, N. Y., 1969, pp 165–167.

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(17) C. B. Moore, "Fluorescence," G. G. Guilbault, Ed., Marcel Dekker, New York, N. Y., 1967, p 133.

Table I. Experimentally Determined Rate Constant Combinations at 300°K

Molecule	P, msec^{-1} Torr^{-1}	$(PT/R) - 1$	PS/R, Torr	$k_h \times 10^{-7}$, M^{-1} sec^{-1} [a]
Ethylene	$49 \pm 4 \times 10^{-4}$	0.019 ± 0.009	14.9 ± 2.0	0.0092
Butene-1	$550 \pm 200 \times 10^{-4}$	0.376 ± 0.020	2.5 ± 0.6	0.104
Isobutylene	$>750 \times 10^{-4}$	<0.56	<1.4	>0.141

[a] Ignoring direct triplet quenching, k_f (see text).

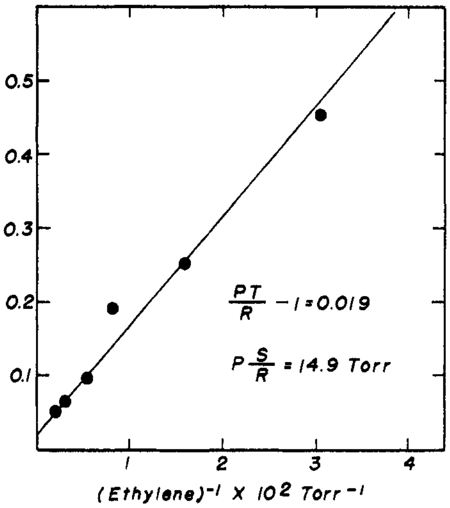

Figure 4. Plot for determination of the sets of rate constants $(PT/R) - 1$ and PS/R for glyoxal ${}^3A_u$ in ethylene.

the experiments, a plot of $\{P - [\Delta\lambda/(E)]\}^{-1}$ against (E) should be linear. On the other hand, if Q is negligible, a plot of $\{P - (\Delta\lambda/(E)]\}^{-1}$ against $[E]^{-1}$ should be linear. The first plot is decidedly nonlinear while the second is relatively linear. Thus it may be concluded that Q is negligible. The above plot is not convenient for accurate determination of interesting rate constants. Instead, since Q may be neglected, eq 2′ may be arranged to give

$$\{[P(E)/\Delta\lambda] - 1\}^{-1} = (PS/R)(E)^{-1} + [(PT/R) - 1] \qquad (2'')$$

A plot of the left-hand side of eq 2″ against $(E)^{-1}$ for ethylene is shown in Figure 4. The slope and intercept allow reasonably reliable determination of the quantities PT/R and PS/R. Similar logic may be applied to the butene-1 data shown in Figure 2. For isobutylene, it is not possible to go to sufficiently low pressures to obtain even an estimate for P. However, some information may be obtained as follows. A lower limit for P may be found from the lowest pressure data point. If Q is neglected and if (E) is sufficiently large that S/T(E) is small, then

$$\Delta\lambda \cong [P - (R/T)](E) + RS/T^2 \qquad (3)$$

Figure 3 does show such a linear behavior. The slope of the points in Figure 3, σ, is $\sigma \cong P - RT$ and the intercept is $\mathscr{I} \cong RS/T^2$. Then $[(PT/R) - 1] \cong [1 - (\sigma/P)]^{-1} - 1$ and $PS/R \cong (PT/R)^2(\mathscr{I}/P)$. From the lower limit for P, an upper limit for PT/R and PS/R may be determined.

The constants obtained in the above manner for each of the three additives are summarized in Table I. The dashed curves in Figures 1, 2, and 3 are computed from eq 2 or eq 3 and the constants in Table I.

D. Relation to Molecular Rate Constants. If the kinetic model indeed describes the observed relaxation, we may make a number of observations concerning the molecular rate constants.

a. $k_h''(E) \ll k_h'(E)^2$ in the pressure range studied for all three additives considered here. Thus decomposition of the intermediate H to give glyoxal ${}^3A_u$ is primarily collisional under the conditions of these experiments.

b. It has been shown that Ar and other inert gases are quite inefficient in quenching glyoxal ${}^3A_u$.[12] It is therefore reasonable to expect k_f is negligible under the conditions used here. Thus $P \cong k_h$, and the cross sections for formation of H in collisions with ethylene, butene-1, and isobutylene may be estimated as 2.2×10^{-5}, 36×10^{-5}, and 50×10^{-5} Å^2, respectively. It is possible that k_f is not negligible, particularly if direct photochemical reaction of glyoxal with ethylene takes place. If so, some revision of the conclusions stated here would be necessary.

c. It may be noted that $(PT/R) - 1 = (k_hk_h')^{-1}(k_f + k_h)(k_h' + k_w - k_f - k_h) - 1$. If k_f is neglected relative to k_h and if $(k_f + k_h)$ is neglected relative to $(k_h' + k_w)$, then $k_w/k_h' \cong (PT/R) - 1$. In any case, this is expected to give an upper limit to k_w/k_h'. It would thus appear that for ethylene, collision-induced photochemistry of H is less than 2% as effective as collisional dissociation yielding glyoxal ${}^3A_u$. On the other hand, these two rates appear to be more comparable for butene-1 and isobutylene, which behave somewhat similarly. If it is assumed that k_h' can be no greater than the molecular collision rate, $k_w < 217$, 2.85×10^3, and 4.25×10^3 msec^{-1} Torr^{-1} for ethylene, butene-1, and isobutylene.

d. $(k_hk_h')^{-1}(k_f + k_h)(k_h'' + k_t - k_0) = PS/R$. Again, if k_f and $(k_h'' - k_0)$ may be neglected, $PS/R \cong k_t/k_h'$. This gives the approximate additive pressure at which the rate constant for collisional decomposition of H equals the rate constant for unimolecular reaction of H. If k_h' is no greater than the molecular collision rate, the unimolecular lifetime of H must be longer than 5.9, 53, and 94 nsec for ethylene, butene-1, and isobutylene. It should be emphasized, however, that k_h' can be quite different for each collision partner; thus ordering of k_t cannot be inferred from the data.

e. The ratio of (PS/R) to $[(PT/R) - 1]$ is roughly k_t/k_w. This ratio is $\sim 7.8 \times 10^2$ Torr for ethylene and $\sim 0.07 \times 10^2$ Torr for butene-1. Thus photochemical reaction of the intermediate formed in glyoxal ${}^3A_u$-additive collisions is primarily unimolecular in the case of ethylene, while it appears to be both unimolecular and bimolecular in the case of butene-1.

It is important to examine the assumption that $|4\beta\gamma(\alpha - \eta)^{-2}| < 1$. From the above arguments, it appears reasonable to neglect k_h'', k_f, and (at least for ethylene) k_w. Thus $4\beta\gamma(\alpha - \eta)^{-2} \cong 4k_hk_h'(E^2)[(k_0 - k_t) + (k_h - k_h')(E)]^{-2}$. If $(k_0 - k_t)$ is small compared to $(k_h - k_h')(E)$, then $4\beta\gamma(\alpha - \eta)^{-2} \cong 4k_hk_h'(k_h - k_h')^{-2}$ which is always small so long as k_h is different from k_h'. On the other hand, if $(k_0 - k_t)$ is large compared to $(k_h - k_h')(E)$, then $4\beta\gamma(\alpha - \eta)^{-2} \cong 4k_hk_h'\cdot(E)^2/(k_0 - k_t)^2$ which also must be small. So apparently only if $k_h \sim k_h'$ so that $4\beta\gamma(\alpha - \eta)^{-2} \sim 4k_h^2\cdot(E)^2(k_0 - k_t)^{-1}$ could the approximation be unjustified; only under these conditions could double-exponential relaxation be clearly evident.

Discussion

From the above arguments then, it is clear that the observed decay rates for *trans*-glyoxal ^3A_u in certain olefins at 300°K are consistent with the existence of a collisionally accessible intermediate state or complex, with lifetimes which may be much longer than 94 nsec, from which both collision-induced and unimolecular photochemical decay may take place. It is important to inquire as to the nature of this state or complex.

Glyoxal has available other electronic states (^1A_u and cis states) which are collisionally accessible on energetic grounds. However, failure to observe the effects reported here for rare gases, NO, or O_2 as collision partners would seem to rule these out as possible intermediates, unless interaction with olefins is most unusual.

The photochemical data suggest two possibilities for a bimolecular complex between n,π^* states of glyoxal and olefins: (1) a biradical intermediate which may collapse to form an oxetane, or (2) a charge-transfer (C-T) complex which may collapse to form a biradical. The observed rates for complex formation (shown in Table I in units of M^{-1} sec^{-1}) are slower by one to two orders of magnitude than those attributed to C-T complex formation in the quenching of triplet butyrophenone in solution by a number of more complex olefins.[4] However, this may not be surprising in view of the relative simplicity of the olefins employed here. The order of the rates of formation is that which would be expected for formation of a π complex between an olefin and an electrophilic molecule. However, the ordering is also that expected for diradical stability.

The existence of unimolecular decay may be easily rationalized in the case of a C-T complex, since the complex may phosphoresce to a dissociative ground state. True unimolecular cyclization of a biradical intermediate to form an oxetane is more difficult to visualize since the triplet must be converted into a singlet. Other cleavage processes are possible, however.

It is observed that collisional photochemical change of the proposed complex competes favorably with dissociation to form glyoxal ^3A_u and olefin for butene-1 while it does not for ethylene. This behavior might be expected for collapse of the C-T complex to form a biradical, since the secondary radical is more stable than the primary one. However, the biradical intermediate might also exhibit such behavior since the reverse of the biradical formation reaction would be faster for ethylene than for butene-1.

From the above discussion it is clear that the present experiments cannot unambiguously distinguish between a C-T intermediate and a biradical one. Further experiments with additional olefins as well as photochemical studies and steady-state phosphorescence studies may shed further light on this problem.

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