Table VI. Ionic Collision Radii

Ion	σ, Å	$\sigma - 1.9$, Å	Rel size
CH_5^+	3.4	1.5	1.0
H_3O^+	2.9	1.0	0.7
NH_4^+	3.3	1.4	0.9
H_3S^+	3.4	1.5	1.0
CF_3^+	3.5	1.6	1.1

In this paper and its predecessor,[2] we have made measurements and calculations on five ionic complexes with methane, namely, those involving the ions CH_5^+, H_3O^+, NH_4^+, H_3S^+, and CF_3^+. Our electrostatic considerations adequately account for the initially surprising variations in the enthalpies of reaction for the formation of the several complex ions, and the overall behavior may be considered to be largely understood, namely, as resulting from classical ion-induced dipole interactions.

We can use these results to obtain approximate values for the sizes of the several ions investigated. The σ value for methane is 3.8 Å, and we take half this value as the collision radius in methane. When this collision radius is subtracted from the σ values obtained for the several ionic complexes, we obtain the collision radius for the ion, and these values and their relative magnitudes are tabulated in Table VI.

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Triplet Yield Determinations of Aromatic Compounds

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Abstract: Triplet yields have been determined for pyrazine, monofluorobenzene, *m*-difluorobenzene, and toluene-α,α,α-d_3, using modified forms of the Cundall and biacetyl methods. For pyrazine, determinations were done at several wavelengths, covering both the $n\pi^*$ and $\pi\pi^*$ states. For all cases except that of pyrazine in the $n\pi^*$ state, there is good agreement between the two methods. Both the discrepancy in the one case of pyrazine and the general applicability of these modified procedures are discussed.

Before 1962, when Ishikawa[1,2] developed the photosensitized emission of biacetyl technique, the determination of the efficiency of the intersystem crossing process (ϕ_T) in the vapor phase remained, for the most part, an unanswered question. In 1963, Cundall[3] used the photosensitized isomerization of olefins technique to determine this quantity. To date, there have been numerous papers on the calculation of ϕ_T, particularly for benzene and benzene-type molecules[3-17] based on one or both of these methods.

Despite their obvious popularity, both methods have their attendant disadvantages.[18] Main among these in the Cundall method are interpretation of data and the high pressures of olefin needed to catch all the donor triplet which adversely causes vibrational relaxation. In the biacetyl method there may be a significant quenching of the singlet donor state,[19] thus making interpretation of the results complicated.

Despite the obvious disadvantages of these methods, they are currently the most versatile at the experimenter's disposal.[20] To shed more light on the validity and applicability of these methods, we have investigated several aromatic compounds differing significantly in their structure and substituents.

Experimental Section

Chemicals. *cis*- and *trans*-2-butene were Phillips research grade. The only impurities consisted of 0.048% trans in cis and 0.001% cis in trans, as determined and checked regularly by glc. Biacetyl (Matheson Coleman and Bell) was purified by preparative gas chromatography at 100° using a 20% SE-30 column and doubly distilled *in vacuo*.

m-Difluorobenzene (Eastman Organic Chemicals) was purified as previously described.[21] Monofluorobenzene (Eastman Organic Chemicals) and pyrazine (Aldrich Chemical Co.) were purified as

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(1) H. Ishikawa and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **84**, 1502 (1962).

(2) H. Ishikawa and W. A. Noyes, Jr., *J. Chem. Phys.*, **37**, 583 (1962).

(3) R. B. Cundall, F. G. Fletcher, and C. C. Milne, *Trans. Faraday Soc.*, **60**, 1146 (1964).

(4) R. B. Cundall and T. F. Palmer, *ibid.*, **56**, 1211 (1960).

(5) R. B. Cundall and C. C. Milne, *J. Amer. Chem. Soc.*, **83**, 3902 (1961).

(6) R. B. Cundall, F. G. Fletcher, and C. C. Milne, *J. Chem. Phys.*, **39**, 3536 (1963).

(7) R. B. Cundall and A. S. Davies, *Trans. Faraday Soc.*, **62**, 1151 (1966).

(8) M. Tanaka, M. Kato, and S. Sato, *Bull. Chem. Soc. Jap.*, **39**, 1423 (1966).

(9) D. Phillips, *J. Chem. Phys.*, **46**, 4679 (1967).

(10) D. Phillips, *J. Phys. Chem.*, **71**, 1839 (1967).

(11) I. Unger, *ibid.*, **69**, 4284 (1965).

(12) F. W. Ayer, F. Grein, G. P. Semeluk, and I. Unger, *Ber. Bunsenges. Phys. Chem.*, **72**, 282 (1968).

(13) G. P. Semeluk, R. D. S. Stevens, and I. Unger, *Can. J. Chem.*, **47**, 597 (1969).

(14) S. L. Lem, G. P. Semeluk, and I. Unger, *ibid.*, **47**, 4711 (1969).

(15) S. L. Lem, G. P. Semeluk, and I. Unger, *ibid.*, **49**, 1567 (1971).

(16) B. H. Scholz and I. Unger, *ibid.*, **48**, 2324 (1970).

(17) R. B. Cundall and W. Tippett, *Trans. Faraday Soc.*, **66**, 350 (1970).

(18) W. A. Noyes, Jr., and D. A. Harter, *J. Chem. Phys.*, in press.

(19) W. A. Noyes, Jr., and I. Unger, *Advan. Photochem.*, **4**, 49 (1966).

(20) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, London, 1970.

(21) T. L. Brewer, *J. Phys. Chem.*, **75**, 1233 (1971).

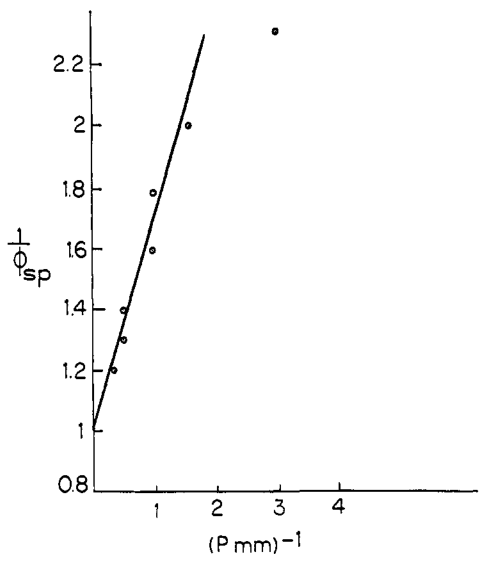

Figure 1. The relative inverse-sensitized emission yield of biacetyl as a function of the inverse of the biacetyl pressure (mm) for the irradiation of pyrazine at 313.0 nm with low biacetyl pressures at room temperature.

previously described.[22,23] Their purities were checked on a Perkin-Elmer flame ionization chromatograph utilizing a 50-ft MBMA[24] capillary column for the former and a 3 × 50 ft column for the latter. All analyses were done at room temperature and indicated no impurities. Toluene-α,α,α-d_3 (Merck Sharp and Dohme, Canada) was used as received.

Prior to use, all compounds were thoroughly degassed by the freeze–thaw method. All experiments were carried out using grease-free mercury-free vacuum lines, equipped with oil-diffusion pumps. Valves were of the Hoke 417 and 413 type. Pressures were measured on Wallace and Tiernan gauges, previously calibrated against an oil manometer.

For the biacetyl work, a 2.5-kW mercury–xenon high-pressure, point source lamp (Hanovia, Inc.), in connection with a Bausch and Lomb grating monochromator Model 33-86-40 with linear reciprocal dispersion of 1.6 nm/mm with 1-mm slits, served as the source of exciting radiation. A quartz lens rendered the light beam parallel through a rectangular quartz cell with dimensions of 2 × 2 × 8 cm. The emission was viewed at right angles to the excitation beam *via* a 1P28 photomultiplier, placed 0.5 cm from the front surface of the cell. A Corning filter No. 3-72 was placed between the cell and the photomultiplier to cut out reflected light. The transmitted light was monitored by an RCA 935 photodiode. The spectral response of the photodiode was checked by a Charles Reader Co. thermopile. The signal outputs from the photomultiplier and photodiode were fed into a Keithley 410 micro-micro ammeter and the signal voltages so produced displayed on a Hewlett-Packard 680 pen recorder.

For the Cundall method, the light source consisted of a 1-kW mercury–xenon high-pressure, point source lamp Type 976C (Hanovia, Inc.) in connection with a Jarrell-Ash 0.25-m grating monochromator, with a linear reciprocal dispersion of 3.2 nm/mm. For excitation at 313.0 nm, the slit widths were 0.5 mm, and at all lower wavelengths they were 2 mm with the exception of the 267-nm work on monofluorobenzene where they were 0.5 mm. The cylindrical quartz reaction cell (5.3 cm long × 2.4 cm diameter) was completely filled with a parallel beam of light. Reflected light, from a quartz plate positioned at 45° to the incident light, used to monitor the incident intensity, was detected by a RCA 935 photodiode. The transmitted light was detected by another, identical photodiode. The signals from these transducers were recorded as described earlier. The system was standardized by use of the actinometer of Hatchard and Parker[25,26] incorporating the modification of Baxendale.[27] Due attention to the errors involved in calculating absorbed light intensities from measurement of transmitted light intensities was given.[28,29]

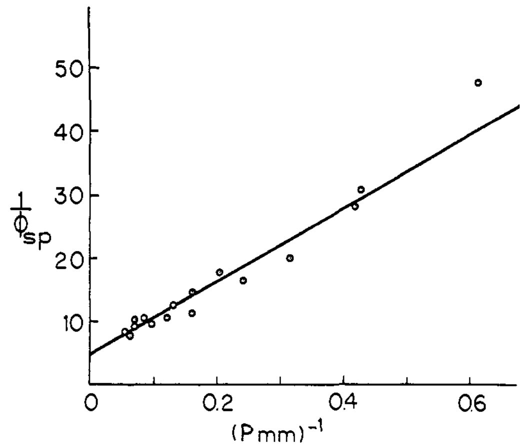

Figure 2. The relative inverse-sensitized emission yield of biacetyl as a function of the inverse of the biacetyl pressure (mm) for the irradiation of pyrazine at 267.0 nm at room temperature.

All reactants were allowed to mix thoroughly before reaction. Overnight mixing was used for the higher pressures.

The contents of the reaction cell, after irradiation, were frozen down into a 25-ml flask, equipped with a silicone rubber septum connected *via* a Cajon coupling. After warming to room temperature, and equilibrating to atmospheric pressure with air, an aliquot was removed and analyzed on an Aerograph Hi-Fi Model 600c flame ionization gas chromatograph, using 2 × 20 ft AG/DEG on 60–80 mesh Chromosorb P columns operated at room temperature. The retention times of the two butene isomers were trans, 20 min, cis, 45 min; thus excellent separation was achieved. Peak areas were calculated by both planimetry and disk integration. The agreement between two methods was better than 1%. An error in the chromatograph attenuator was corrected by adding 10.5% to the apparent concentration since the gc attenuator was nonlinear on the different ranges needed to record the high and low concentrations of the olefins.

In all experiments, the pressure of the aromatic compound was 1 mm or less. In all figures, the method of least squares was used to determine the intercepts.

Results

Biacetyl Method. The biacetyl method was used to determine the triplet yields of pyrazine, *m*-difluorobenzene, and toluene-α,α,α-d_3. The sensitized emission yields from biacetyl were determined as a function of pressure and are displayed in Figures 1–7 for the various aromatic donors studied. In the case of pyrazine, which, interestingly, has two electronic states in the accessible uv region, a wavelength dependence of the triplet yield was also investigated. These results for the different wavelengths studied, 313.0, 267.0, 264.0, and 252.0 nm, are shown in Figures 1–4, respectively, in which $1/\phi_{sp}$ is plotted as a function of $1/p$ where ϕ_{sp} is the relative sensitized emission yield of biacetyl as determined by the photomultiplier/phototube responses and p is the pressure in millimeters.

Figure 5 is a graphical representation of the data for *m*-difluorobenzene at 264.0 nm which shows $1/\phi_{sp}$ as a function of biacetyl pressure. The dashed line is an extrapolation of the high-pressure data to zero pressure.

Figure 6 also displays the results of the *m*-difluorobenzene investigation but is a plot of $1/\phi_{sp}$ *vs.* $1/p$ for the low-pressure data only.

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[22] K. Nakamura, *J. Chem. Phys.*, **53**, 998 (1970).

[23] K. Nakamura, *J. Amer. Chem. Soc.*, **93**, 3138 (1971).

[24] MBMA is a mixture of *m*-bis(*m*-phenoxyphenoxy)benzene and Apiezon L grease.

[25] C. A. Parker, *Proc. Roy. Soc., Ser. A*, **220**, 104 (1953).

[26] C. G. Hatchard and C. A. Parker, *ibid.*, **235**, 518 (1956).

[27] J. H. Baxendale and N. K. Bridge, *J. Phys. Chem.*, **59**, 783 (1955).

[28] J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1967.

[29] S. H. Jones and K. Salisbury, *Photochem. Photobiol.*, in press.

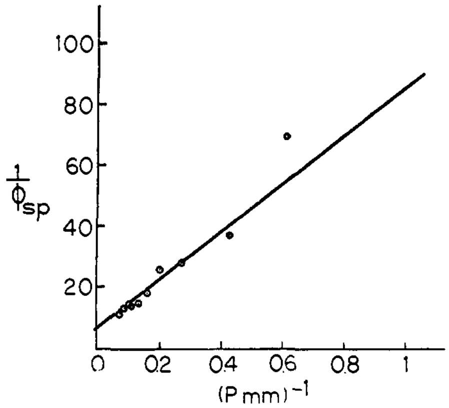

Figure 3. The relative inverse-sensitized emission yield of biacetyl as a function of the inverse of the biacetyl pressure (mm) for the irradiation of pyrazine at 264.0 nm at room temperature.

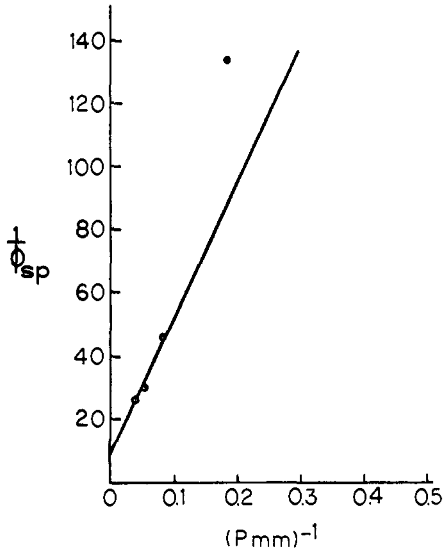

Figure 4. The relative inverse-sensitized emission yield of biacetyl as a function of the inverse of the biacetyl pressure (mm) for the irradiation of pyrazine at 252.0 nm at room temperature.

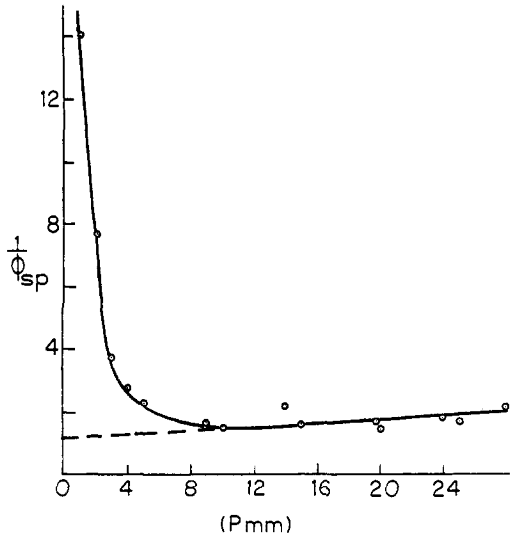

Figure 5. The relative inverse-sensitized emission yield of biacetyl as a function of the biacetyl pressure (mm) for the irradiation of *m*-difluorobenzene at 264.0 nm at room temperature.

Figure 7 is a $1/\phi_{sp}$ *vs.* $1/p$ plot of the toluene-α,α,α-d_3 results which were obtained at 264.0 nm.

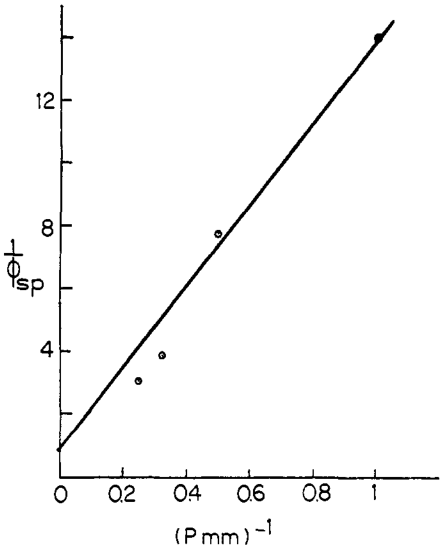

Figure 6. The relative inverse-sensitized emission yield of biacetyl as a function of the inverse of the biacetyl pressure (mm) for the irradiation of *m*-difluorobenzene at 264.0 nm with low biacetyl pressures at room temperature. (The lower pressure points have been given more weighting than the higher pressure data since the latter occur close to the inflection of the curve and are thus less representative.)

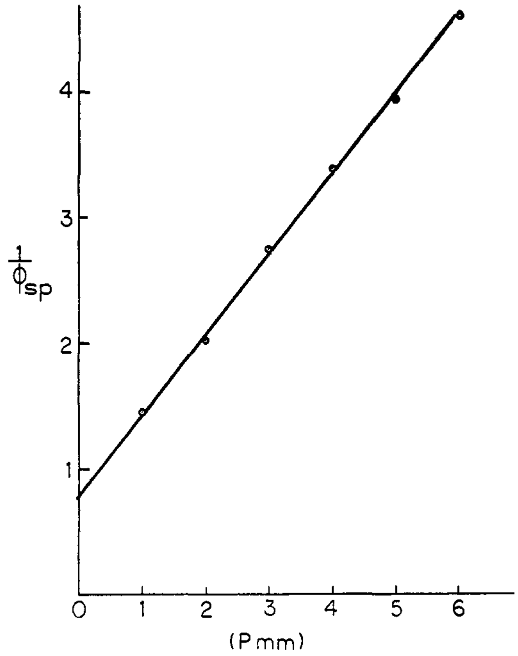

Figure 7. The relative inverse-sensitized emission yield of biacetyl as a function of the biacetyl pressure (mm) for the irradiation of toluene-α,α,α-d_3 at 266.0 nm at room temperature.

In all cases the pressure of the aromatic compound was adjusted to allow 15–20% absorption which amounted to 1 mm or less since the compounds were all strong absorbers.

The absolute values of the triplet quantum yield were calculated from the intercepts of the graphs (see Discussion for a discussion of the calculations) using the emission of biacetyl to standardize the system. In this way, it is not necessary to know or assume a triplet quantum yield for some external standard, such as benzene or biacetyl, and thus the absolute

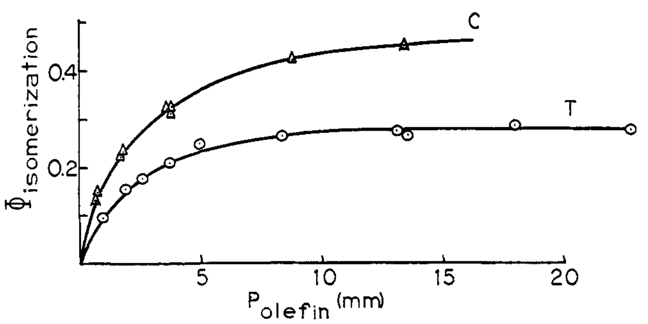

Figure 8. The isomerization of 2-butenes as a function of their pressures, sensitized by pyrazine irradiated at 313.0 nm at room temperature.

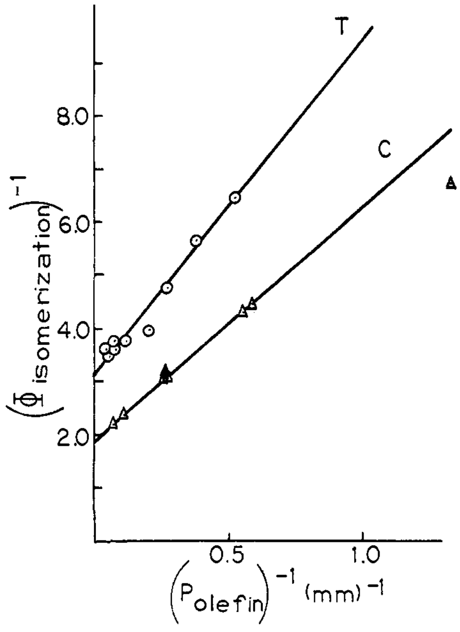

Figure 9. The inverse of the isomerization quantum yields of 2-butenes as a function of the inverse of their pressures, sensitized by pyrazine irradiated at 313.0 nm at room temperature.

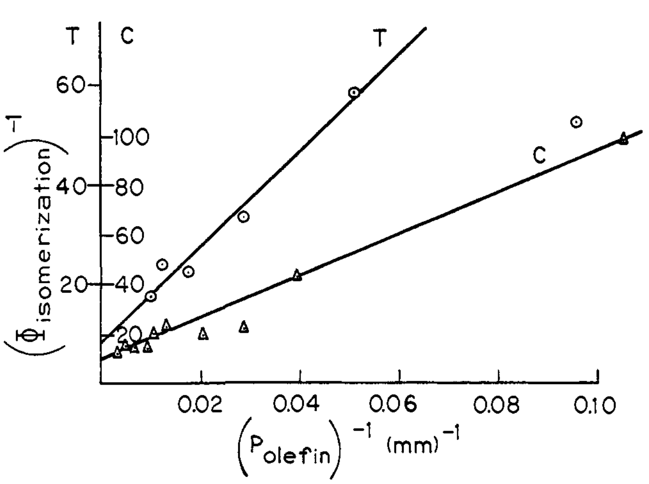

Figure 10. The inverse of the isomerization quantum yields of 2-butenes as a function of the inverse of their pressures, sensitized by pyrazine irradiated at 264.0 nm at room temperature.

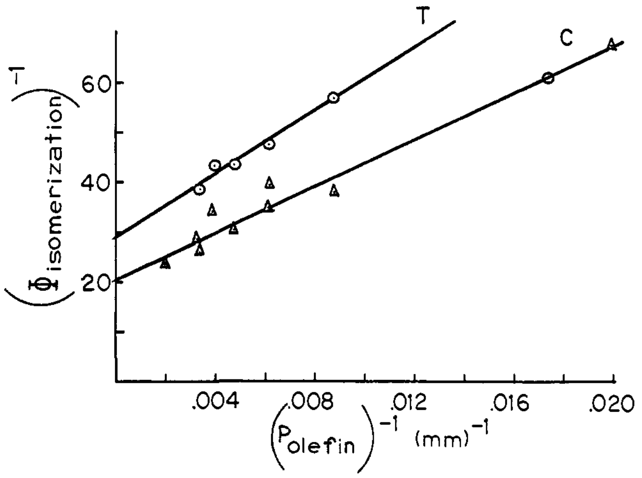

Figure 11. The inverse of the isomerization quantum yields of 2-butenes as a function of the inverse of their pressures, sensitized by pyrazine irradiated at 248.0 nm at room temperature.

Table I. Photostationary State [c-B/t-B]$_{PSS}$ for Pyrazine Irradiated at 313.0 nm

Run	Duration, sec	[c-B/t-B]$_{initial}$	[c-B/t-B]$_{final}$
PS1	3,600	0.782	0.83
PS2	14,400	1.39	1.17
PS3	21,600	1.35	1.15
PS4	14,400	1.05	1.09
PS5	7,200	0.90	0.967

error should be lowered. The values of the triplet yields obtained are shown in Table II.

Cundall Method. The Cundall method was used to determine the triplet yield of pyrazine and monofluorobenzene. The sensitized isomerization yields of both 2-butene isomers were determined as a function of the 2-butene isomer pressure for each compound.

Pyrazine. The isomerization yields for pyrazine sensitization were determined at 313.0, 264.0, and 248 nm. Figure 8 shows the respective isomerization yields of each isomer *vs.* its concentration at 313.0 nm, while Figure 9 is a reciprocal plot of these parameters from which the isomerization yield at infinite olefin concentration (ϕ_{isom}) is calculated. Figures 10 and 11 display the inverse parameters (again for each 2-butene isomer) for excitation at 264.0 and 248.0 nm, respectively. Figures 12 and 13 show the variation of the sensitized isomerization yield with the pressure of *cis*- and *trans*-2-butene isomer, respectively, again in reciprocal form, for monofluorobenzene as the sensitizer (exciting wavelength, 267 nm).

Table I shows the variation of the (*cis*-2-butene/*trans*-2-butene) ratio as a function of the irradiation time for the pyrazine system irradiated at 313.0 nm. The calculated extrapolated ratio at infinite time can be related to the photostationary state (PSS) and this quantity is discussed more fully in the following section. In order to avoid long exposure times, a mixture of isomers close to the ratio thought to be the PSS ratio was prepared and the ratio recalculated after irradiation. The PSS was approached from both sides, and it can be seen that it changes only slightly after ~6 hr of photolysis. Owing to the rather shorter lifetime of pyrazine in the $\pi\pi^*$ band and monofluorobenzene at the wavelength studied (as evidenced by the much higher pressures of olefin required in these systems over pyrazine at 313.0 nm), the determination of the PSS for these cases was not attempted.

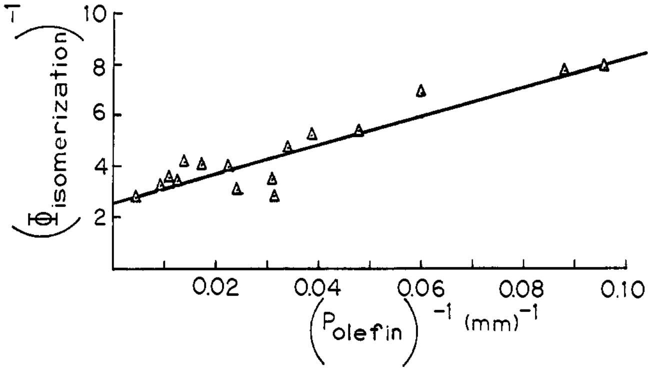

Figure 12. The inverse of the isomerization quantum yields of *cis*-2-butene as a function of the inverse of *cis*-2-butene pressure sensitized by monofluorobenzene at 267.0 nm at room temperature.

Discussion

Biacetyl Method. The following equations are thought to be the most important in the kinetics of this method.

$A_0 + h\nu \longrightarrow {}^1A_1$	I_a
${}^1A_1 \longrightarrow A_0 + h\nu_f$	k_1
${}^1A_1 \longrightarrow A_0$	k_2
${}^1A_1 \longrightarrow {}^3A_1$	k_3
${}^3A_1 \longrightarrow A_0$	k_4(a)
${}^3A_1 \longrightarrow A_0 + h\nu_p$	k_4(b)
${}^3A_1 + \text{BiA} \longrightarrow A_0 + {}^3\text{BiA}$	k_5
${}^1A_1 + \text{BiA} \longrightarrow A_0 + {}^1\text{BiA}^{\text{II}}$	k_6
${}^1A_1 + \text{BiA} \longrightarrow A_0 + {}^1\text{BiA}^{\text{I}}$	k_7
${}^1\text{BiA}^{\text{I}} \longrightarrow {}^3\text{BiA}$	k_8
${}^3\text{BiA} \longrightarrow \text{BiA}$	k_9
${}^3\text{BiA} \longrightarrow \text{BiA} + h\nu_p$	k_{10}

Here, A_0 represents a sensitizer molecule in its ground electronic state, ${}^1A_1$ represents the molecule in its first-excited singlet state. ${}^3A_1$ represents A in its first-excited triplet state. ${}^1\text{BiA}^{\text{I}}$ represents the acceptor (biacetyl) in its first-excited singlet state, and ${}^1\text{BiA}^{\text{II}}$ is biacetyl in its second-excited singlet state. The other symbols are self-explanatory.

The usual steady-state treatment of the mechanism yields the following equation

$$\phi_{\text{sp}} = \frac{k_{10}}{k_9 + k_{10}}\left[\frac{k_7[\text{BiA}] + k_5k_3[\text{BiA}]/(k_4 + k_5[\text{BiA}])}{k_1 + k_2 + k_3 + (k_6 + k_7)[\text{BiA}]}\right] \qquad \text{(I)}$$

where ϕ_{sp} is the sensitized emission yield of biacetyl and $k_4 = k_4\text{(a)} + k_4\text{(b)}$.

This equation can be simplified somewhat by considering only the high-pressure or the low-pressure experimental regions.

Considering first the low-pressure region, where k_6[BiA] and k_7[BiA] are relatively unimportant, eq I can be reduced to

$$1/\phi_{\text{sp}} = [(k_9 + k_{10})/k_{10}](1/\phi_t{}^0) + [(k_9 + k_{10})/k_{10}\phi_t{}^0](k_4/k_5[\text{BiA}]) \qquad \text{(II)}$$

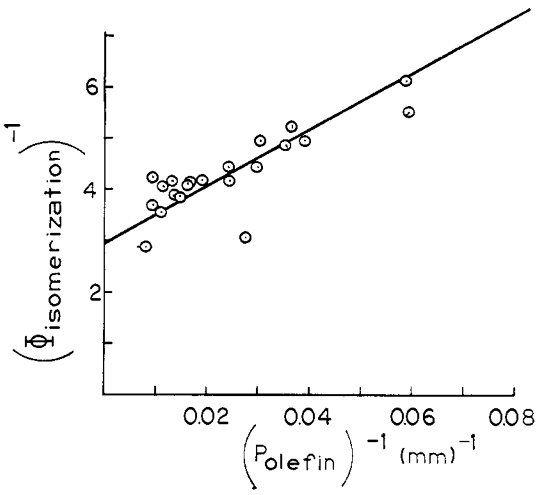

Figure 13. The inverse of the isomerization quantum yields of *trans*-2-butene as a function of the inverse of *trans*-2-butene pressure sensitized by monofluorobenzene at 267.0 nm at room temperature.

where $\phi_t{}^0 = k_3/(k_1 + k_2 + k_3)$ and is the triplet yield of the donor in the absence of biacetyl. Thus a plot of $1/\phi_{\text{sp}}$ *vs.* 1/[BiA] should give an intercept of $(k_9 + k_{10})/k_{10} \cdot (1/\phi_t{}^0)$.

In the high-pressure region, where $k_5[\text{BiA}] \gg k_4$, eq I becomes

$$1/\phi_{\text{sp}} = \frac{k_9 + k_{10}}{k_{10}}\left[\frac{k_1 + k_2 + k_3}{k_7[\text{BiA}] + k_3} + \frac{(k_7 + k_6)[\text{BiA}]}{k_7[\text{BiA}] + k_3}\right] \qquad \text{(III)}$$

Neglecting k_7[BiA] for the moment, eq III can be further simplified to

$$1/\phi_{\text{sp}} = \frac{k_9 + k_{10}}{k_{10}}\left[\frac{1}{\phi_t{}^0} + k_6/k_3[\text{BiA}]\right] \qquad \text{(IV)}$$

In this case, a plot of $1/\phi_{\text{sp}}$ *vs.* [BiA] should be linear with an intercept of $[(k_9 + k_{10})/k_{10}](1/\phi_t{}^0)$ *i.e.*, the same as that of eq II. Of course, the plot would be valid only if k_7 is unimportant. Although k_7 has been shown to be important in certain cases,[18,30] it does not seem to be the case in this work since the present data do seem to follow eq IV. These results are certainly expected in the case of pyrazine since the total singlet quenching is small.[31] Even when the singlet quenching is important, as in toluene-α,α,α-d_3, the contribution of k_7 to the overall singlet quenching must be negligible, as evidenced by the excellent linearity of the plot (see Figure 7). In addition, as can be seen from Table II, the triplet yields calculated from the high-pressure data (*i.e.*, in the region where singlet energy transfer is becoming important) are in excellent agreement with those from the low-pressure region (*i.e.*, where singlet energy transfer is negligible). Thus, the validity of this treatment is reinforced.

Previous workers utilizing the biacetyl method have relied upon an absolute value for $k_{10}/(k_{10} + k_9)$, which is usually taken to be 0.145.[32] Not withstanding the fact that a more recent determination of this quantity[33]

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(30) K. Nakamura, *J. Chem. Phys.*, 54, 4160 (1971).

(31) S. H. Jones and T. L. Brewer, *J. Phys. Chem.*, 75, 3769 (1971).

(32) G. M. Almy and P. R. Gillette, *J. Chem. Phys.*, 11, 188 (1943).

(33) A. Horowitz and J. G. Calvert, *J. Amer. Chem. Soc.*, in press.

Table II. Triplet Yields by the Biacetyl and Cundall Methods

Compound	Biacetyl method[a]			Cundall method[a]				
	Wavelength, nm	ϕ_T(HP)	ϕ_T(LP)	Wavelength, nm	ϕ_{CT}	ϕ_{TC}	ϕ_{CT}/ϕ_{TC}	ϕ_T
Pyrazine	313	1.04	0.96	313	0.53	0.34	1.60	0.87[b]
	267		0.198	264	0.11	0.12	0.92	0.23
	264		0.142	248	0.048	0.035	1.37	0.081
	252		0.095					
Monofluorobenzene	265[c]	0.81		267	0.39	0.34	1.14	0.73
m-Difluorobenzene	264	0.75	0.75					
	274[d]	0.77						
Toluene-α,α,α-d_3	266	0.68						
Undeuterated toluene	266[f]	0.66		266.8[e]				0.70

[a] All values ±10%. [b] As discussed, this does not, in reality, represent a triplet yield but simply the sum of $\phi_{CT} + \phi_{TC}$. [c] See ref 30. [d] See ref 12. [e] See ref 41. [f] See ref 14.

essentially is in agreement with the earlier work, the method used in the present work is considered more reliable since an absolute value of $k_{10}/(k_9 + k_{10})$ is not required. Thus, many of the problems inherent in determining absolute emission yields[32] are obviated. The method presented simply involves the standardization of the photosystem with biacetyl and the calibration of the phototube *via* a thermopile. Thus all data can be related to a relative biacetyl emission yield, simply monitored by an arbitrary reading on the photomultiplier tube. As an example, starting with pure biacetyl, a ratio between emitted light (photomultiplier) and absorbed light (phototube) is determined for excitation at 435.8 nm. The irradiation is carried out in the presence of a sensitizer at a wavelength where only the sensitizer absorbs, and the photomultiplier/phototube ratio is again determined after the phototube reading has been corrected for its wavelength response characteristics. If the sensitizer has a unit triplet yield, then this latter ratio will be the same as that determined with pure biacetyl at 435.8 nm. If the triplet yield is less than unity, then the ratio of these two determinations will give the value of the triplet yield. In summary, the modified biacetyl method presented here offers several distinct advantages over that used by all other workers. First, it is not necessary to capture all of the triplet donor state in order to calculate a triplet yield. Second, in many cases, both high- and low-pressure data can be obtained, and, accordingly, two independent determinations of the triplet yield can be compared. Third, it is not necessary to assume an absolute value for the biacetyl emission yield, nor is a secondary standard necessary.

Cundall Method. A mechanism[34] which seems to successfully explain the results of this method for most benzene-type aromatic sensitizers is shown here.

$$A_0 + h\nu \longrightarrow {}^1A_1 \tag{A}$$

$${}^1A_1 \longrightarrow A_0 + h\nu_f \tag{B}$$

$$\longrightarrow A_0\ \text{(isomer)} \tag{C}$$

$$\longrightarrow A_0\ \text{(heat)} \tag{D}$$

$${}^1A_1 + M \longrightarrow A_0 + M \tag{E}$$

$${}^1A_1 \longrightarrow {}^3A_1 \tag{1}$$

$${}^1A_1 + M \longrightarrow {}^3A_1 + M \tag{1'}$$

$${}^3A_1 \longrightarrow A_0 + \text{heat} \tag{2}$$

$${}^3A_1 + M \longrightarrow A_0 + M \tag{2'}$$

$${}^3A_1 \longrightarrow A_0 + h\nu_p \tag{2''}$$

$${}^3A_1 + \text{c-B} \longrightarrow A_0 + {}^3\text{c-B} \tag{3c}$$

$${}^3A_1 + \text{t-B} \longrightarrow A_0 + {}^3\text{t-B} \tag{3t}$$

$${}^3A_1 + Q \longrightarrow A_0 + {}^3Q \tag{3q}$$

$$\begin{tikzcd}
{}^3\text{c-B} \arrow[r, shift left, "k_{4c}"] \arrow[d, "k_{5c}"'] & {}^3\text{t-B} \arrow[l, shift left, "k_{4t}"] \arrow[d, "k_{5t}"] \\
\text{c-B} & \text{t-B}
\end{tikzcd}$$

The symbols are the same as those for the biacetyl method with the following additions. c-B refers to a ground-state *cis*-2-butene molecule, t-B to a ground-state *trans*-2-butene molecule. ^{3}c-B and ^{3}t-B are their first-excited triplet states, respectively. From this scheme, the following results emerge

$$\phi_{CT}/\phi_{TC} = k_{4c}k_{5t}/k_{4t}k_{5c} = \text{branching ratio} \tag{V}$$

where ϕ_{CT} is the initial quantum yield of isomerization of cis to trans and ϕ_{TC} is that for trans to cis. (This assumes $k_{3c}[\text{c-B}]$ and $k_{3t}[\text{t-B}] \gg k_2 + k_2'' + k_2'[M] + k_{3q}[Q]$ which is true at infinite olefin pressure.)

The photostationary state (*i.e.*, the photoequilibrium that exists between the two butene isomers) is obtained from the *equilibrium rates of* isomerization.

The result shown below follows directly by taking $d(\text{c-B})/dt = 0$ or $d(\text{t-B})/dt = 0$.

$$\left[\frac{\text{t-B}}{\text{c-B}}\right]_{\text{PSS}} = \frac{k_{3c}}{k_{3t}}\left[\frac{k_{5t}k_{4c}}{k_{5c}k_{4t}}\right] = \frac{k_{3c}}{k_{3t}}\left[\frac{\phi_{CT}}{\phi_{TC}}\right] \tag{VI}$$

From eq VII and VIII it can be seen that plots of $[\phi_{\text{isom}}]^{-1}$ *vs.* $[p_{\text{olefin}}]^{-1}$, similar to those of Figure 9, can be constructed.

$$\begin{aligned} 1/\phi_{CT} = {} & (1/\phi_T)[(k_{4c}k_{5t} + k_{5c}k_{4t} + k_{5c}k_{5t})(k_2 + k_2'' + \\ & k_2'[M])/(k_{5t}k_{4c}k_{3c})](1/[\text{c-B}]) + \\ & (1/\phi_T)[(k_{4c}k_{5t} + k_{5c}k_{4t} + k_{5c}k_{5t})/k_{5t}k_{4c}] \end{aligned} \tag{VII}$$

$$\begin{aligned} 1/\phi_{TC} = {} & (1/\phi_T)[(k_{4c}k_{5t} + k_{5c}k_{4t} + k_{5c}k_{5t})(k_2 + k_2'' + \\ & k_2'[M])/k_{5c}k_{4t}k_{3t}](1/[\text{t-B}]) + \\ & (1/\phi_T)[(k_{4c}k_{5t} + k_{5c}k_{4t} + k_{5c}k_{5t})/k_{5t}k_{4c}] \end{aligned} \tag{VIII}$$

The sum of the intercepts from (VII) and (VIII) gives $(1/\phi_T)[2 + \text{BR} + 1/\text{BR}]$, where BR is the branching ratio, if $k_{4c} \gg k_{5c}$ and $k_{4t} \gg k_{5t}$.

As the mechanism indicates, the branching ratio, although not required to be unity, should be a function of the olefin only. However, in the case of pyrazine sensitization at 313.0 nm, the branching ratio of 1.6 is significantly different from the value of approximately unity found with the majority of sensitizers.[19,34] This immediately suggests that the simple mechanism presented here is inadequate for the interpretation of the results of pyrazine. Thus the simple addition of the two extrapolated isomerization yields may not give the triplet yield *per se*. Presently, it is not clear whether these results indicate that the Cundall mechanism proceeds *via* a more complicated process (*e.g.*, complex mechanism[35]) or that pyrazine is an exception, possibly due to its relatively low-lying triplet state. Cohen and Goodman[36] have calculated the energy levels of the lower lying singlet and triplet states of pyrazine. Both the $\pi\pi^*$ triplet (80.9 kcal mol^{-1}) and the nπ^* triplet (76.0 kcal mol^{-1}) are of lower energy than the nπ^* singlet state (86.4 kcal mol^{-1}). Although initially intersystem crossing should lead to the $\pi\pi^*$ triplet, the nπ^* triplet is most likely the one involved in energy transfer since the internal conversion between the two triplet states is extremely fast.[36,37]

The triplet energy levels of the 2-butenes are not known with a high degree of accuracy. Determinations of the triplet energy level of *cis*-2-butene by the oxygen perturbation method[38] and electron-scattering method[39] put this level at 78.22 and 76 kcal mol^{-1}, respectively, and since the trans isomer is thermodynamically more stable, the electronic excitation energy for the trans may well be higher. Thus it may be that with pyrazine, energy transfer to the *cis*-2-butene is occurring according to the simple kinetic scheme above, and the transfer to the trans isomer is more complicated due to the larger endothermicity. Assuming this postulate to be correct, the pyrazine triplet yield could be determined by multiplying ϕ_{CT} by $[1 + \phi_{\mathrm{TC}}/\phi_{\mathrm{CT}}]$ where $\phi_{\mathrm{TC}}/\phi_{\mathrm{CT}}$ is the branching ratio obtained with high-energy sensitizers.[34] Thus, $\phi_{\mathrm{T}} = 0.53(1 + 1/1.02) = 1.05$. Since irradiation of pyrazine in the $\pi\pi^*$ state results in a branching ratio of approximately unity, the complications above are not present, and use of the Cundall method seems valid. Presumably this is due to population of a higher energy nonemitting triplet.[40] From Table II it can be seen that except for the pyrazine results at 313.0 nm, there is excellent agreement between the Cundall and biacetyl methods. In fact, in the wavelength study on pyrazine in the $\pi\pi^*$ band, the agreement is surprising, since it would be expected that the relatively high pressures of 2-butene needed to catch the triplet would also cause some vibrational relaxation, resulting in a higher triplet yield compared to the biacetyl method. Tentatively, this agreement may be indicative of a rapid intersystem crossing process. Since the quantum yields of fluorescence, polymerization, and isomerization are 0,[23] $\sim 5 \times 10^{-2}$,[40] and $\sim 5 \times 10^{-3}$,[40] respectively, it appears reasonable that ϕ_{ISC} should be indeed a rapid but relatively inefficient process, since the quantum yields are only of the order of 0.1–0.2.

The present results, in general, are in good agreement with previous determinations as indicated in Table II. In particular, the results on *m*-difluorobenzene are in good agreement with those of Unger,[12] in spite of the fact that the earlier fluorescence data were inaccurate, as has been pointed out.[21] In addition, the results with toluene-α,α,α-d_3 show good correlation with undeuterated toluene results determined by the biacetyl method[14] and also show fair correlation with those by the Cundall method.[41] These results lend support to the idea that the methyl hydrogen vibrational modes are unimportant in the excited-state decay processes of aromatic compounds.[42]

The study of monofluorobenzene was repeated, since an earlier determination[10] was based on a branching ratio of 1.37[6] instead of the correct branching ratio of 1.02. The author has pointed this out in a recent redetermination of this value and gets a value of $\phi_{\mathrm{T}} = 0.82$ using the 1.02 value.[43] However, the redetermination was based on benzene as a secondary standard, and the results reported here rely on chemical actinometry as a primary standard. Despite these differences, the agreement between the two values is reasonable, the main discrepancy lying in the different branching ratios which should not be a function of actinometry.

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(34) E. K. C. Lee, H. O. Denschlag, and G. A. Hanninger, Jr., *J. Chem. Phys.*, 48, 4547 (1968).

(35) N. J. Turro, *Photochem. Photobiol.*, 9, 555 (1969).

(36) B. J. Cohen and L. Goodman, *J. Chem. Phys.*, 46, 713 (1967).

(37) M. A. El-Sayed, *Accounts Chem. Res.*, 1, 8 (1968).

(38) G. P. Semeluk and D. D. S. Stevens, *Can. J. Chem.*, 49, 2452 (1971).

(39) H. H. Brongersma, J. A. v.d. Hart, and L. J. Osterhoff, "Fast Reactions and Primary Processes in Chemical Kinetics," S. Claesson, Ed., Interscience, New York, N. Y., 1967.

(40) M. Magat, N. Ivanhoff, F. Lahmani, and M. Pileni, "Transitions Non Radiatives dans les Molecules," *J. Chim. Phys.*, 20$^{\mathrm{e}}$ Réunion de la Société de Chimie Physique, Paris, May 1969, p 212.

(41) C. S. Burton and W. A. Noyes, Jr., *J. Chem. Phys.*, 49, 1705 (1968).

(42) T. E. Martin and A. H. Kalantar, *Chem. Phys. Lett.*, 4, 235 (1969).

(43) Kh. Al-Ani and D. Phillips, private communication.