Benzene Photosensitization and Direct Photolysis of Cyclohexanone and Cyclohexanone-2-*t* in the Gas Phase[1]

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Abstract: A mechanistic diagnosis of the photodecomposition and photoisomerization of cyclohexanone by benzene photosensitization is reported. C_5-hydrocarbon products (1-pentene and cyclopentane) have a singlet origin, while the isomeric product (5-hexenal) has a triplet precursor. Cyclohexanone quenches the excited singlet benzene ($^1B_{2u}$) with a $\pi\sigma^2$ cross section of $\sim$50 Å^2, as compared to its quenching cross section for the triplet benzene ($^3B_{1u}$) of $\sim$1 Å^2. Wavelength effect (248–313 nm) and pressure effect of added foreign gases ($\sim$200–1 Torr) on the product distribution in the direct photolysis have been studied. The C_5-hydrocarbon quantum yields increase with increasing photoactivation energy and decrease with increasing deactivator gas pressure. The 5-hexenal quantum yield decreases with increasing photoactivation energy and is invariant over the pressure range studied. A photochemical mechanism consistent with the present as well as the previous findings is proposed. Importance of the $S_1 \rightsquigarrow T_1$ intersystem crossing is stressed.

Benzene photosensitization studies of cyclobutanone[3] and cyclopentanone[4] in recent years have clarified some important mechanistic questions raised about direct photolysis of these simple cyclic ketones.[5] Furthermore, a careful reexamination of the direct photolysis of cyclobutanone with respect to the variations of the exciting wavelength and of the added foreign gas pressure led to the proposal of a photochemical transformation mechanism involving a vibrationally hot, ground electronic state intermediate ($S_0{}^*$).[6] Therefore, we have carried out a study of benzene photosensitization and direct photolysis of cyclohexanone, in spite of the existing reports on the latter.[7–11] Since the photochemistry of cyclohexanone has been extensively reviewed,[12] and since an interesting reexamination of the mechanism based on the photolysis of 2-methylcyclohexanone has appeared recently,[13] its further review is avoided here.

Experimental Section

Chemicals. Cyclohexanone (Baker and Adamson) and cyclobutanone (Aldrich Chemical) were used after drying with Drierite ($CaSO_4$) under vacuum, and these purified samples had no detectable impurity according to gas chromatographic analysis. The preparation of α-labeled tritiated ketone has been described elsewhere.[3b] The specific activity of the first prepared sample of cyclohexanone-2-*t* was 0.027 mCi/mmol, and the value for the second preparation was 0.004 mCi/mmol. Zone-refined grade benzene (99.999%, Litton Chemicals), research grade propane and *cis*-2-butene (Phillips Petroleum Co.), *cis*-1,3-pentadiene (Chemical Samples Co.), and spectroquality *c*-C_6H_{12} (Matheson Coleman and Bell) were used after degassing at liquid nitrogen temperature. O_2 (99.5% minimum, National Compressed Gas Co.) was used directly.

Vacuum and Photochemical Apparatus. A mercury-free and grease-free vacuum line identical with that used for cyclobutanone photolysis work[6] was used. A small photolysis cell of 80.9-ml volume and 50-mm optical path, and a large photolysis cell of 479-ml volume and 149-mm optical path were used. Both cells were equipped with two flat 50-mm o.d. Suprasil quartz windows, a cold finger at the bottom of the cylindrical cell body, and a grease-free valve.

Photolysis at 253.7 nm was carried out using a low-pressure mercury lamp (Mineralight R-51, Ultra-Violet Products, Inc.) equipped with a Corning CS 7-54 filter and a D_3P solution filter (10 mm thick, 200 mg/l. of 2,7-dimethyl-3,6-diazacyclohepta-2,6-diene perchlorate, Peninsular Chemresearch, Inc.).[14] Light intensity was 0.7–1.0 × 10^{16} quanta/sec for 12-cm^2 area. Photolysis at wavelengths other than 253.7 nm, selecting only intense lines (248, 280, 290, 297, 302, and 313 nm), was carried out using a small monochromator (Bausch and Lomb, MgF_2 coated uv grating, 3.2 nm/mm reciprocal dispersion) equipped with a 200-W superpressure mercury lamp (Osram, HBO-200).[6] Particularly for the photolysis at 248 nm, a D_3P solution filter was used in addition. Because the extinction coefficient of cyclohexanone is small at 248 nm and the intensity of the mercury line is low at this wavelength, the chromatic impurity in the 280–310-nm region from scattering can affect the photolysis results without appropriate filtering. All of the photolysis runs were made at room temperature (23°).

Product Analysis. Hydrocarbon products were analyzed typically on a radio gas chromatographic setup, as described elsewhere.[15] Radiochemical assay was not always carried out, since the analytical data obtained were poor due to the low specific activity of the cyclohexanone-2-*t* used. Therefore, as much as half of the data was obtained by the measurement of the macroscopic gc peak areas. Two dimethylsulfolane columns (35% by weight, 0.25-in. o.d. × 60 ft and 0.188-in. o.d. × 25 ft) were used at room temperature. A Carbowax 20M column (5% by weight, 0.25-in. o.d. × 10 ft plus 0.188-in. o.d. × 40 ft) was used at 135° for the analysis of benzene, aldehyde, and ketone. Samples were handled in a manner similar to that described elsewhere.[4]

Chemical Actinometry. Quantum yields of the products in the benzene-photosensitized runs were determined by the Cundall method used earlier.[3,16,17] The quantum yields in the benzene–

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Table I. Wavelength Dependence of the Product Distribution in the Direct Photolysis of Cyclohexanone[a]

Run no.	λ_{ex}, nm	Photolysis time, min	Product yields, μmol 1-Pentene	Cyclopentene	5-Hexenal	HA/C5[b]
308 (309)	313	60	0.028	~0.011	(0.23)	5.9
311 (310)	313	60	0.028	~0.011	(0.21)	5.4
312 (313)	302	120	0.065	0.033	(0.12)	1.2
314 (315)	302	120	0.064	0.031	(0.12)	1.3
324 (325)	297	120	0.154	0.067	(0.14)	0.6
327 (328)	297	120	0.161	0.053	(0.13)	0.6
316 (317)	289	180	0.156	0.067	(0.054)	0.3
318 (319)	289	180	0.164	0.060	(0.066)	0.3
320 (321)	280	180	0.214	0.109	(~0.024)	~0.07
322 (323)	280	180	0.127	0.050	(~0.009)	~0.05
354 (355)	253.7	180	0.235	0.142	(~0.014)	~0.04

[a] All samples contained 1.00 Torr of cyclohexanone in a 479-ml cell. [b] C5 = PE + CP, where PE is 1-pentene and CP is cyclopentane; HA is 5-hexenal.

cyclohexanone mixture were evaluated on the basis of the *external actinometry* data thus obtained.

Quantum yields of the products in the direct photolysis runs were determined by an *internal comparison actinometry* as described below. Quantum yields of the hydrocarbon products (ethylene, propylene, and cyclopropane) in the photolysis of cyclobutanone vapor ($P < 50$ Torr) have been recently measured over the wavelength range of 265.4–313.0 nm,[18] and the overall quantum yield of the hydrocarbon products adds up to a constant value of 1.0 within the accuracy of the measurement. All of these products arise from unimolecular decomposition processes, and furthermore their relative quantum yields measured over wide ranges of added gas pressures and wavelength indicate that the overall quantum yield must be unity below 10 Torr and in the wavelength range of ~248–320 nm.[6] Therefore, we have carried out direct photolysis of the cyclohexanone–cyclobutanone mixtures below a few Torr of total pressure and then evaluated the quantum yields of 1-pentene and cyclopentane produced by the photolysis of cyclohexanone. This procedure is valid as long as the product yields resulting from the cyclohexanone photolysis are not affected by the presence of cyclobutanone in the same photolysis cell and *vice versa*. The quantum yield data obtained in this manner, using the product yield ratio, the parent concentrations, and the measured molar absorptivity values for the parent ketones at each photolysis wavelength, are probably accurate to ~20%. This degree of accuracy is certainly satisfactory for the present study, since the quantum yield measurements by other direct methods will be so impractical due to the low vapor pressure of cyclohexanone at 23° (~3 Torr) and the low molar absorptivity values of cyclohexanone in the wavelength region of 240–320 nm ($\epsilon_{max} \approx 14$ l. mole^{-1} cm^{-1} at λ 293 nm). The values of the molar absorptivity used in the computation have been reported elsewhere.[8,19]

Results

(A) Direct Photolysis

Wavelength Dependence. The effect of the photoactivation wavelength on the product distribution was studied at 1.0 Torr cyclohexanone pressure between 313 (91 kcal/mol) and 253.7 nm (113 kcal/mole), and the results are shown in Table I. The ratio of the 5-hexenal yield (HA) to the C_5-hydrocarbon yield (C5) varies over two orders of magnitude, and it is as low as 0.04 at 253.7 nm, indicating that the elimination of CO is very efficient compared to the photoisomerization to aldehyde at high excitation energy. In order to assess overall product quantum yield over this wavelength range, the quantum yields of 1-pentene (PE) and cyclopentane (CP) were measured at low pressure by photolyzing an equimolar mixture of cyclohexanone and cyclobutanone. The quantum yield of 5-hexenal was conveniently estimated from the yield ratio of HA/PE observed at each wavelength as shown in Table I. The individual as well as the total product quantum yields thus obtained are shown in Table II. The total quantum yield (Φ_{total}) becomes lower than unity at 289 nm and gradually decreases to a value as low as 0.4 at 313 nm; it is near unity below 280 nm within the accuracy of the measurement, 10–20%.

Table II. Wavelength Dependence of the Product Quantum Yields for Cyclohexanone Photolysis in the Cyclohexanone–Cyclobutanone Mixture[a]

Run no.	λ_{ex}, nm	CP/PE	Φ_{PE}	Φ_{CP}	Φ_{HA}[b]	Φ_{total}
351	313		~0.04	<0.03	0.30	~0.42
352	313		~0.05	<0.03	0.34	~0.42
349	302	0.3	0.15	0.05	0.28	0.48
350	302	0.4	0.15	0.06	0.28	0.49
347	297	0.3	0.27	0.09	0.23	0.59
348	297	0.4	0.23	0.09	0.20	0.52
345	289	0.4	0.44	0.19	0.15	0.78
346	289	0.5	0.49	0.23	0.18	0.90
343	280	0.34	0.71	0.24	0.08	1.03
344	280	0.39	0.60	0.23	0.07	0.90
353	253.7	0.65	0.49	0.32	<0.03	~0.84
354	253.7	0.61	0.54	0.33	<0.03	~0.90
361	248	0.67	0.48	0.32	<0.03	~0.83

[a] All samples contained 1.00 Torr each of cyclohexanone and cyclobutanone in a 479-ml cell, and they were irradiated for 2 to ~4.5 hr. [b] This value was estimated by multiplying the observed Φ_{PE} value by a ratio, HA/PE, determined at each excitation wavelength as shown in Table I.

Pressure Dependence. The effect of the pressure of added foreign gases on the product distribution has been examined in detail at only two photolysis wavelengths, 297 and 253.7 nm. We have not attempted a detailed study at wavelengths longer than 297 nm, because the C_5-hydrocarbon quantum yield is so low as to give yield data of poor accuracy. The pressure quenching of the 1-pentene yield by added c-C_6H_{12} in the 297-nm photolysis is clearly shown in Table III. However, the pressure quenching of the 5-hexenal yield by c-C_6H_{12} at 297 nm is only minor, even at 10 Torr. Since the aldehyde yields were determined to an accuracy of 5–10%, the slight decrease observed with the increasing pressure may not be real.

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Table III. Effect of Added $c\text{-}C_6H_{12}$ on the Ratio of 5-Hexenal/1-Pentene in the Direct Photolysis of Cyclohexanone at 297 nm[a]

Run no.	Pressure of $c\text{-}C_6H_{12}$, Torr	Photolysis time, min	Product yields (μmol) 1-Pentene	Product yields (μmol) 5-Hexenal	HA/PE
324 (325)	0	120	0.116[b]	0.104[b]	0.9
327 (328)	0	120	0.121[b]	0.098[b]	0.8
332 (333)	2.0	120	0.096[b]	0.093[b]	1.0
334 (335)	4.0	90	0.074	0.080	1.1
336 (337)	6.0	90	0.062	0.087	1.4
338 (339)	8.4	90	0.055	0.093	1.7
340 (341)	10.0	90	0.055	0.087	1.6

[a] All samples contained 1.00 Torr of cyclohexanone in a 479-ml cell. [b] Product yields have been normalized to those irradiated for 90 min.

Table IV. Relative Quantum Yields at Low Cyclohexanone Pressures[a]

Run no.	Wavelength, nm	Pressure of cyclohexanone, Torr	Photolysis time, min	Φ_{rel}[b] PE	Φ_{rel}[b] CP	Φ_{rel}[b] HA	CP/PE
408	~300	1.00	120	8.3	3.2		0.38
409	~300	0.50	180	8.7	3.3		0.37
411	~300	0.25	360	11.1	4.7		0.42
410	~300	0.10	900	11.4	4.5		0.40
414	313	2.00	60			0.68	
416	313	1.00	90			0.61	
417	313	0.50	180			0.58	

[a] A 479-ml photolysis cell was used. A combination of 297- and 302-nm mercury lines of roughly equal intensity was used for the ~300-n m photolysis. [b] Relative quantum yields were calculated by normalizing the observed yields for the cyclohexanone pressure and photolysis time only.

The pressure quenching of the 1-pentene and cyclopentane yields by added C_3H_8 and O_2 in the 253.7-nm photolysis is shown in Figure 1. The relative quantum yields were measured either in pure cyclohexanone from 0.05 to 2.0 Torr, or with 2.0 Torr of cyclohexanone to which varying amounts of either C_3H_8 or O_2 were added. Since the 5-hexenal yield is very small at this wavelength, it was not determined as a function of total pressure. It is quite obvious that the sum of the quantum yields of 1-pentene and cyclopentane is invariant up to 40-Torr propane pressure, while the former increases with increasing C_3H_8 pressure at the expense of the latter. However, both of the hydrocarbon quantum yields suffer reduction above 40 Torr of propane. The quenching effect of O_2 is different from that of C_3H_8 in that O_2 scavenges both hydrocarbon products. This difference is further illustrated by the ratio of CP/PE in the upper half of Figure 1.

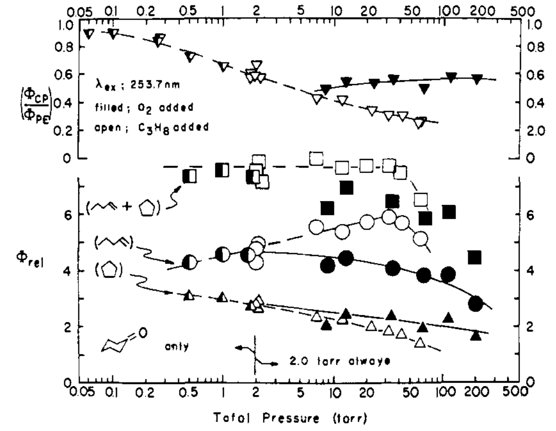

Figure 1. Pressure dependence of relative quantum yields of the C_6 products at 253.7 nm: open, C_3H_8 added; filled, O_2 added; half-filled, no additive gas present in a large cell.

It was also found at 297 nm that 95 Torr of added C_3H_8 and O_2 to 2.0 Torr of cyclohexanone quenched the 1-pentene yield to 0.16 and 0.17 of the original value, respectively; furthermore, the cyclopentane yield was quenched correspondingly. However, the aldehyde yield was essentially unaffected by the addition of 95 Torr of O_2. This result is consistent with the results shown in Table III.

Below 1.0 Torr of cyclohexanone, there are trends for increasing the hydrocarbon quantum yield in the 300-nm photolysis and for decreasing the aldehyde quantum yield in the 313-nm photolysis, as shown in Table IV. However, these trends are of minor importance.

(B) Benzene Photosensitization

Pressure Dependence. Benzene photosensitization of cyclohexanone gives substantial yields of 1-pentene and cyclopentane above 1 Torr and a comparable yield of 5-hexenal below 1 Torr. An appreciable fraction of the C_5-hydrocarbon yield arises from the direct photolysis of cyclohexanone at 253.7 nm, and therefore the sensitized quantum yields of the hydrocarbon products were evaluated after subtracting this fraction from the observed yield.[3,4] Such a correction was not necessary for the 5-hexenal yield because the quantum yield of this product from direct photolysis at 253.7 nm is nearly negligible as shown in Table VI. However, an appreciable "secondary photosensitization" of 5-hexenal was unavoidably realized due to an abnormally high conversion in the low-pressure runs; therefore, the yield of the secondary photosensitization product (1,3-butadiene and acetaldehyde) was added to the observed 5-hexenal yield in order to obtain the "corrected" sensitized 5-hexenal yield (primary yield) Φ_{HA}'. The results of the sensitized quantum yields measured from 0.05 to 3.0 Torr cyclohexanone pressure are shown in Tables V and VI. Stern–Volmer plots applicable to the benzene photosensitization systems[3,4] were composed from the above data, and they are shown in Figures 2 and 3.

Table V. Hydrocarbon Product Distribution *vs.* Pressure of Cyclohexanone-2-*t* in the Benzene-Photosensitized Runs[a]

Run no.	P_{CHT}, Torr	1-Pentene yields, μmol Total[b]	Sensitized[c]	Φ_{PE}'	Cyclopentane yields, μmol Total[b]	Sensitized[c]	Φ_{CP}'
272	0.05	0.016	0.015	0.0093	0.005	0.004	0.0029
262	0.05	0.018	0.017	0.0104	0.007	0.006	0.0036
271	0.067	0.018	0.016	0.0105	0.007	0.006	0.0040
261	0.10	0.026	0.023	0.0144	0.012	0.010	0.0064
269	0.125	0.032	0.029	0.0185	0.013	0.011	0.0069
254	0.15	0.044	0.040	0.0176	0.024	0.022	0.0097
260	0.20	0.041	0.036	0.023	0.017	0.014	0.0089
253	0.25	0.075	0.068	0.030	0.034	0.030	0.014
270	0.25	0.050	0.043	0.028	0.021	0.017	0.011
252	0.30	0.072	0.064	0.029	0.041	0.037	0.016
280	0.40	0.069	0.058	0.038	0.031	0.025	0.016
275	0.50	0.081	0.068	0.044	0.039	0.032	0.020
277	0.70	0.099	0.080	0.052	0.051	0.040	0.026
276	1.00	0.140	0.113	0.073	0.057	0 041	0.026
281	1.50	0.181	0.141	0.091	0.072	0.048	0.031
278	2.00	0.217	0.164	0.106	0.092	0.061	0.039
279	3.00	0.284	0.205	0.132	0.113	0.065	0.042

[a] All of the photolysis runs were made for 15 min at 253.7 nm with a 479-ml cell. [b] Observed total yield arising from both direct and sensitized photolysis. [c] Sensitized = total − direct.

Table VI. Corrected 5-Hexenal Yield *vs.* Pressure of Cyclohexanone-2-*t* in the Benzene-Photosensitized Runs[a]

Run no.	P_{CHT}, Torr	$\frac{100 \times HA}{HA + CH}$	Yields, μmol 5-Hexenal	Butadiene	N,[d] μmol	Cor Φ_{HA}
267 (272)	0.05	3.9	0.050	(0.020)	1.54	0.046
231 (262)	0.05	4.2	0.054	(0.028)	2.01	0.041
266 (271)	0.067	3.8	0.066	(0.018)	1.54	0.055
230 (261)	0.10	3.7	0.096	(0.024)	2.01	0.059
265 (269)	0.125	3.2	0.101	(0.018)	1.54	0.078
323 (254)	0.15	3.4	0.138	(0.022)	2.01	0.080
248 (260)	0.20	2.7	0.137	(0.019)	1.98	0.079
227 (253)	0.25	2.3	0.150	(0.026)	1.99	0.088
130 (026)[b]	0.25	5.4	0.059	(0.014)	1.81 (0.57)	~0.059
234 (252)	0.30	2.2	0.168	(0.016)	2.00	0.092
126 (016)[b]	0.30	5.2	0.068	(0.016)	1.81 (0.57)	0.066
119[b]	0.40	4.8	0.084	(0.015)[c]	1.64 (0.57)	~0.078
117 (017)[b]	0.50	4.2	0.091	(0.014)	1.64 (0.57)	~0.080
111 (024)[b]	1.00	3.3	0.142	(0.017)	1.75 (0.57)	0.111
116 (021)[b]	1.50	2.9	0.192	(0.010)	1.64 (0.57)	0.134

[a] All of the runs were with 1.00 Torr of benzene in a 479-ml cell for 15 min at 253.7 nm. [b] Benzene (2.5 Torr) was in a 80.9-ml cell instead of a 479-ml cell. [c] An estimated value. [d] An amount of the excited benzene produced by the absorption of 253.7-nm radiation as calculated from a *cis–trans* isomerization monitor run.

The Stern–Volmer plots for the C_5-hydrocarbon yields (Figure 2) are linear above 0.3 Torr but curve downward slightly below this pressure. The half-quenching pressure ($P_{1/2}$) for 1-pentene is 2.5 Torr of cyclohexanone and the limiting sensitized quantum yield extrapolated to infinite pressure (Φ'^{∞}) is only 0.25, with an accuracy of ~20%. The sensitized quantum yield of cyclopentane scatters enough to prevent an

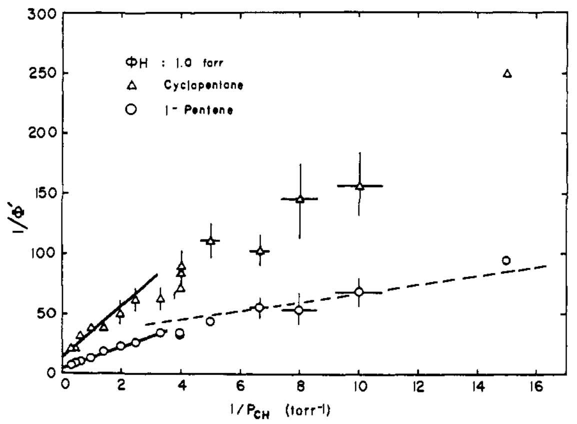

Figure 2. Stern–Volmer plot for the singlet energy transfer. Reciprocal (sensitized) quantum yields of 1-pentene and cyclopentane *vs.* reciprocal pressure of cyclohexanone.

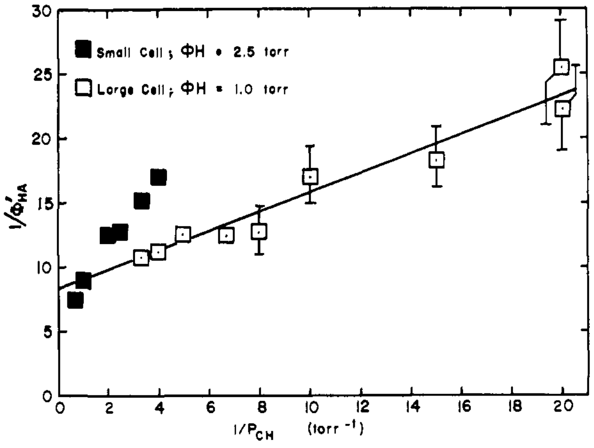

Figure 3. Stern–Volmer plot for the triplet energy transfer. Reciprocal quantum yield (sensitized) of 5-hexenal *vs.* reciprocal pressure of cyclohexanone.

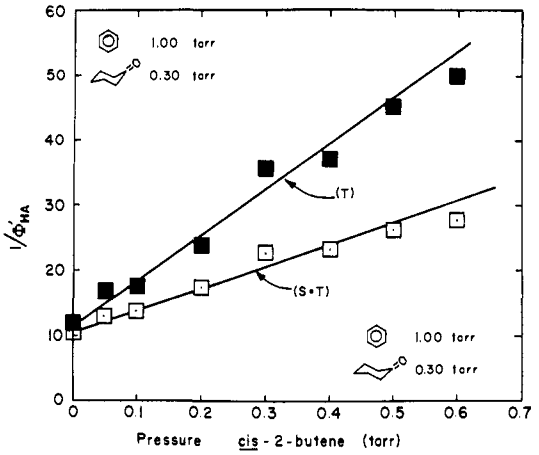

Figure 4. Quenching of the 5-hexenal yield by *cis*-2-butene in the benzene photosensitization system: unfilled squares, observed, sensitized; filled, sensitized triplet only.

accurate determination of the above two sensitization constants, due to the low product yield of cyclopentane; the value of Φ'^{∞} for cyclopentane is $\leqslant 0.1$ and the value of $P_{1/2}$ is $\geqslant 1$ Torr of cyclohexanone. Since the ratio of cyclopentane to 1-pentene is dependent on the total pressure of the system to some extent (see Figure 1), the sensitization constants of the C_5 product should also be evaluated from a Stern–Volmer plot for the sum of the C_5 hydrocarbons. The $P_{1/2}$ and Φ'^{∞} values for the C_5 product are 2.5 Torr and 0.33, respectively. The downward curvature at low cyclohexanone pressure in Figure 2 might be an indication of a minor, additional mechanism for C_5-hydrocarbon formation. Since an accurate value of $P_{1/2}$ for quenching the fluorescence emission of benzene has been measured to be 2.9 Torr of cyclohexanone,[19] which is in reasonable agreement with $P_{1/2} = 2.5$ Torr found above, the C_5-hydrocarbon products *originate in the singlet benzene photosensitization.*

The Stern–Volmer plot for the 5-hexenal yield (Figure 3) is linear below 0.3 Torr of cyclohexanone at low conversion. When an experimental condition for high conversion using a small photolysis cell prevails, the corrected hexenal yield is measurably lower than when it is measured with a large cell. Therefore, the result obtained at high conversion is definitely unreliable and cannot be used any further. The values of $P_{1/2}$ and Φ'^{∞} for the 5-hexenal are 0.09 Torr of cyclohexanone and 0.12, respectively. The $P_{1/2}$ value obtained here for cyclohexanone is comparable to that (0.10 Torr) obtained for cyclobutanone in the triplet benzene sensitization,[3] and to that (0.2 Torr) obtained for 4-pentenal formation from cyclopentanone.[4] Since the $P_{1/2}$ value obtained here is much lower than that for the fluorescence quenching,[19] and since it checks with the values obtained for the triplet benzene sensitization of cyclobutanone and cyclopentanone, 5-hexenal *orginates in the triplet benzene photosensitization.*

It is expected that the addition of *cis*-2-butene to the benzene–cyclohexanone samples will reduce the yield of the triplet-sensitized product (5-hexenal). A Stern–Volmer plot for the quenching by *cis*-2-butene is shown in Figure 4, indicating a substantial reduction of 5-hexenal at 0.6 Torr of *cis*-2-butene. There is a measurable yield from the singlet sensitization which cannot be quenched by *cis*-2-butene effectively,[3] and therefore the overall quenching appears less than what is expected with the triplet sensitization alone. The fraction of the singlet contribution to the overall 5-hexenal yield at 0.30 Torr of cyclohexanone is 0.18 in the absence of *cis*-2-butene, and this fraction increases correspondingly with the increasing pressure of *cis*-2-butene in the system. The corrected plot in which the singlet contribution is taken out is shown as (T) with filled squares.

Discussion

Benzene Photosensitization

Mechanistic diagnosis by benzene photosensitization has been discussed in detail elsewhere,[3-5] and it is necessary here merely to summarize briefly what happens with cyclohexanone. It is clear that an excited singlet cyclohexanone (S_1) is produced by the collisional energy transfer from the $^1B_{2u}$ benzene to the ground-state cyclohexanone and this singlet energy-transfer process predominates at pressures above 1 Torr of cyclohexanone. On the other hand, the triplet energy transfer from the $^3B_{1u}$ benzene producing a triplet cyclohexanone (T_1) predominates below 1 Torr cyclohexanone pressure. The C_5-hydrocarbon products accompanying a CO-elimination process originate largely from the singlet energy-transfer process, while the triplet energy-transfer process gives 5-hexenal almost exclusively as a photoisomeric product.[11,12]

Since the quantum yield of the triplet benzene at 253.7 nm is 0.71 ± 0.06,[3] our value of 0.12 for $\Phi_{HA}'^{\infty}$ sets the quantum efficiency of the 5-hexenal formation by the triplet benzene sensitization (n_T) at $0.12/0.71 \approx 0.17$.[3,4] This implies that $\sim ^8/_{10}$th of the triplet cyclohexanone fails to give an observable product. An upper limit of the C_5-hydrocarbon quantum yield *via* triplet sensitization is estimated as 0.007 at 0.1 Torr of cylohexanone and thus its contribution to the value of n_T is only ≤ 0.02. It is conceivable that the T_1 state produced by the $^3B_{1u}$ benzene ($E_T = 84$ kcal/mol) has an excitation energy of ~80 kcal/mol as in the benzene–cyclobutanone system;[3] as a result, it may fail to photoisomerize and undergoes a radiationless relaxation to an *unreactive state.*

It is unfortunate that a direct photolysis of cyclohexanone cannot be carried out conveniently at ~360 nm (80 kcal/mol), which would correspond to the excitation energy transferred to cyclohexanone by the $^3B_{1u}$ benzene sensitization, because the absorption coefficient of cyclohexanone at this wavelength is too low. Therefore, the most reasonable comparison between the direct and sensitized photolysis can be made for the quantum efficiencies for the product formation observed at 313 nm (direct excitation) and in the $^3B_{1u}$ benzene sensitization. Our value of the quantum yield of 5-hexenal at 313 nm as listed in Table II is 0.32, while the value reported by Srinivasan[11] for comparable experimental conditions is 0.16. At this wavelength, our value probably contains the greater uncertainty, since the extinction coefficients for both cyclohexanone and cyclobutanone were not accurately measurable. The true value of the quantum yield at 313 nm may be close to 0.2, and we will consider this as a more reasonable value than 0.3. It is interesting to note that the lower value of the 5-hexenal quantum yield at 313 nm is nearly equal to the quantum efficiency (n_T) of 0.17 for the formation of 5-hexenal from the triplet energy transfer (from $^3B_{1u}$ benzene). This implies that the $S_1 \rightsquigarrow T_1$ intersystem crossing probably has a quantum yield near unity and also the reverse intersystem crossing ($T_1 \rightsquigarrow S_0$) is rapid enough to have a probable quantum yield of 0.8 at this level of internal excitation. The fact that the 5-hexenal quantum yield in 3-methylpentane solution is 0.11 and that in pure cyclohexanone is 0.27[11] is consistent with the above interpretation based on the results obtained in the near limit of low-energy direct photolysis at 313 nm.

For the singlet sensitization process, we obtain a value of $\Phi_{C_5}'^{\infty} = 0.33$. It is difficult to arrive at an accurate assessment of the 5-hexenal quantum yield originating in the S_1 state. However, if we assume that approximately 95–99 kcal/mol of excitation energy is transferred to cyclohexanone as in the singlet benzene sensitization of cyclobutanone[3] and cyclopentanone,[4] corresponding to a direct excitation at ~290–300 nm, then the ratio of HA/C5 can be estimated as ~0.3–0.6 from Table I. Indeed, this is so at 2.0 Torr of cyclohexanone, as seen in Figure 5. Therefore a reasonable upper limit of the 5-hexenal quantum yield *via* the singlet benzene sensitization can be obtained as 0.2 (see Table II), on the assumption that S_1 from direct photolysis at 290 nm is equivalent to that from the singlet benzene sensitization.[3] Then, the upper limit of the total quantum efficiency of the product formation *via* the singlet benzene sensitization (n_S) is 0.5, and thus $^5/_{10}$th of the S_1 appears to give no product. However, the fraction failing to give a product in the singlet sensitization is definitely less than that fraction found in the triplet sensitization.

The shift of the benzene photosensitization mechanism from predominantly "triplet" at low pressure to predominantly "singlet" at high pressure of cyclohexanone is well illustrated in Figure 5 with the ratio of HA/C5. The ratio of CP/PE is also pressure sensitive; it increases slightly with increasing cyclohexanone pressure up to a few tenths of a Torr, indicating a trend in which the average excitation energy of the precursor is higher at higher pressure where a greater fraction of the precursor comes from the singlet sensitization. This is consistent with the result shown in Table II. Beyond 0.5 Torr of cyclohexanone pressure the trend reverses, showing a slight decrease in the ratio of CP/PE with the increasing total pressure due to a significant increase in the partial pressure of cyclohexanone.

Direct Photolysis

(a) Pressure Effect at 297 nm. The most salient feature of the pressure effect of c-C_6H_{12} gas at 297 nm is that the precursor of 1-pentene (and cyclopentane) is collisionally quenched while the precursor of 5-hexenal is not. A simple two-level mechanism involving the former precursor (Y) for its unimolecular decomposition (D) and its collisional deactivation (S) predicts a linear Stern–Volmer plot of the reciprocal quantum yield of 1-pentene (D^{-1}) *vs.* the pressure of c-C_6H_{12}, if the cyclohexanone pressure is kept at a constant minimum value. Such is the case for the data presented in Table III. The half-quenching pressure of the 1-pentene yield is 7 Torr of c-C_6H_{12} plus 1.0 Torr of cyclohexanone (or a total pressure of 8 Torr). This pressure corresponds to a binary collision frequency of 1.1×10^8 sec^{-1}, if the Lennard-Jones gas kinetic collision diameter of cyclohexanone is assumed to be similar to that of c-C_6H_{12} at room temperature.[20] If the collisional deactivation efficiency of unity is assigned, then the lifetime of this intermediate Y must be $\sim 1 \times 10^{-8}$ sec. Furthermore, the observed linearity of the Stern–Volmer plot requires the monoenergetic nature of the intermediate Y and implies that it has not yet eliminated CO; Y would have a wide internal energy distribution if energy photopartitioning took place by the elimination of CO,[6,21,22] and the plot would exhibit downward curvature. A break down of the strong collision assumption will also give a curved Stern–Volmer plot.[21]

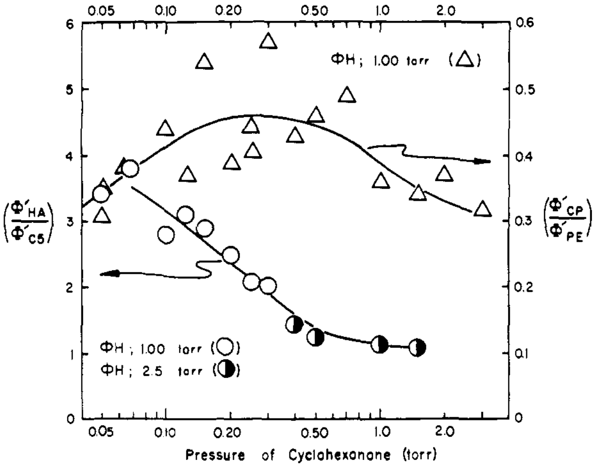

Figure 5. Variation of the product ratios as a function of cyclohexanone pressure in the benzene photosensitization system: left, ratio of 5-hexenal to C_5-hydrocarbon yield; right, ratio of cyclopentane to 1-pentene yield.

The precursor of 5-hexenal (X) must have a lifetime much shorter than 1×10^{-8} sec or it is not affected by collision. Furthermore, the collisional deactivation of the intermediate Y is unlikely to lead to the formation of the intermediate X, since no complementary increase in the 5-hexenal yield was observed to accompany the pressure quenching of the C_5 products. It can thus be hypothesized that the intermediate X could share the same precursor with the intermediate Y.

(b) Pressure Effect at 253.7 nm. It is expected that the lifetimes of the intermediates which undergo unimolecular transformations would shorten appreciably when the photoexcitation energy is increased from 97 kcal/mol at 297 nm to 113 kcal/mol at 253.7 nm. Indeed, the precursor Y generated at 253.7 nm is shorter lived than that at 297 nm by one to two orders of magnitude, since it is beginning to get quenched only above 40 Torr of C_3H_8; below this pressure, the relative quantum yields of the sum of 1-pentene and cyclopentane are constant, as shown in Figure 1. However, the increasing yield of 1-pentene and the corresponding decrease of cyclopentane with the increasing added propane pressure require that both products share the same precursor (Z), which undergoes a unimolecular process

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(20) $\sigma = 6.143$ Å for cyclohexane was taken from J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1964, p 1214.

(21) R. F. Klemm, D. N. Morrison, P. Gilderson, and A. T. Blades, *Can. J. Chem.*, 43, 1934 (1965).

(22) R. J. Campbell and E. W. Schlag, *J. Amer. Chem. Soc.*, **89**, 5103 (1967).

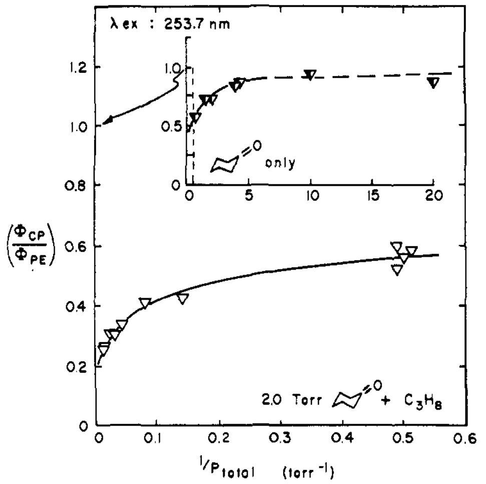

Figure 6. The curved Stern–Volmer plot showing the (CP/PE) ratio *vs.* the reciprocal total pressure when C_3H_8 is added at 253.7 nm.

(*D*) to yield cyclopentane in competition with the collisional stabilization leading to the 1-pentene formation (*S*).

It is expected that the ratio of (*D*/*S*) plotted against $1/\omega$ would be curved downward, where ω is the mean collision frequency, if there is an initial distribution of the unimolecular rate coefficients (k_E's) due to the energy photopartitioning.[3,21] Figure 6 simply illustrates that such is the case. The precursor Z must be absent from the CO group in order to maintain a wide distribution of the internal excitation energy, and it is reminiscent of the *vibrationally hot* cyclopropane produced in the direct photolysis of cyclobutanone.[3,21,22] An interesting point to note is that 1-pentene is produced when the intermediate Z (C_5H_{10}) is collisionally stabilized by C_3H_8, C_3H_6, and *cis*-1,3-pentadiene at the expense of cyclopentane, while the intermediate Z is slowly scavenged away by O_2. We would like to propose that the intermediate Z is most likely to be a pentamethylene-like species ($\dot{C}H_2CH_2CH_2CH_2\dot{C}H_2$)[8] whose distribution of the lifetimes for cyclization is in the time domain of 10^{-5} to $\sim10^{-9}$ sec.

Ground-State Energetics

The following values of enthalpy of formation at 298°K can be used to evaluate the energetics of the various reaction paths available for cyclohexanone:[12a,23] cyclohexanone, −53.1; 5-hexenal, −29.5; CO, −26.42; cyclopentane, −18.5; 1-pentene, −5.00; C_2H_4, 12.50; and C_3H_6, 4.88 kcal/mol. The most energetically favored process is the formation of cyclopentane and CO with an endothermicity of 8.2 kcal/mol, while the next two favored processes are the formation of 1-pentene and CO, requiring 21.7 kcal/mol, and the isomerization to 5-hexenal, requiring 23.6 kcal/mol. The least favored process to form C_2H_4, C_3H_6, and CO requires 44.1 kcal/mol.

Excited State Energetics and Wavelength Effect

The enthalpy of formation at 298°K for the pentamethylene (the intermediate Z, C_5H_{10}) can be estimated as $\sim$57 kcal/mol, while that for the acylpentamethylene (the intermediate Y, $C_5H_{10}CO$) can be estimated as $\sim$22 kcal/mol.[23] Therefore, it is energetically possible to produce the intermediate Z plus CO (84 kcal/mol endothermic) as well as to produce the intermediate Y (75 kcal/mol endothermic), when cyclohexanone is excited by 313-nm radiation (91 kcal/mol). However, the formation of the intermediate Z *via* the triplet benzene sensitization would be nearly thermoneutral or endothermic and it would be extremely inefficient, since the triplet energy of benzene (E_T) is 84 kcal/mol. The formation of the intermediate Y *via* triplet benzene sensitization would be energetically feasible, although the rate could be quite slow. Of course, these processes accompanying the singlet benzene sensitization and the direct excitation at wavelengths shorter than 313 nm will be more efficient. The results shown in Tables I and II are consistent with this interpretation.

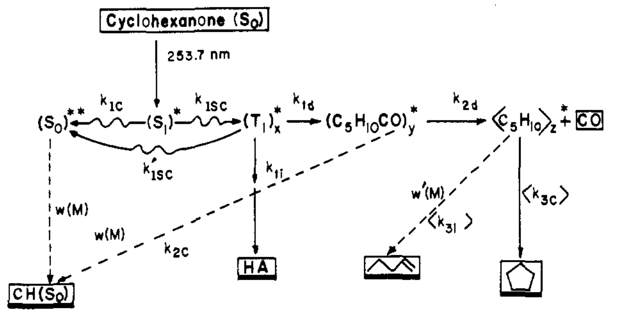

Figure 7. Photochemical transformation mechanism of cyclohexanone.

The overall mechanistic scheme for photochemical transformation of excited cyclohexanone which is consistent with all of these observations is shown in Figure 7. The following summary can clarify the basic features. (1) The intermediate Z, with a wide energy distribution and thus a wide unimolecular rate distribution, can account for the curved Stern–Volmer plot of the (CP/PE) ratio *vs.* $1/P_{total}$ and for the increasing (CP/PE) ratio with the increasing photoactivation energy and with the decreasing pressure or mean collision frequency at 253.7 nm. (2) The intermediate Y, with little or no energy distribution, can account for the linear Stern–Volmer plot of the $1/\Phi_{PE}$ *vs.* pressure of added c-C_6H_{12} ($\leqslant$10 Torr) at 297 nm and for the pressure quenching of the C_5-hydrocarbon products above 40 Torr of propane at 253.7 nm. (3) The intermediate X can unimolecularly either isomerize to 5-hexenal by intramolecular H-atom abstraction (k_{1i}) or undergo a bond rupture of the C_1–C_2 bond (k_{1d}), free of collisional interference; and the (k_{1d}/k_{1i}) ratio increases with increasing photoactivation energy. (4) The short-lived character of the intermediate X as in (3) accounts for the pressure independence of the 5-hexenal yield in excess O_2, C_3H_8, c-C_6H_{12}, etc. (5) The triplet character of the intermediate X can account for the triplet benzene-sensitized production of 5-hexenal, involving an energy transfer of $\sim$80 kcal/mol, and the Hg($^3P_1$)-sensitized production of hydrocarbons plus CO, involving energy transfer of presumably over 100 kcal/mol.[24] (6) The

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[23] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rogers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

[24] (a) See footnote 24 of ref 13 about the unpublished work of F. P. Lossing and J. B. Homer on the mercury-sensitized photolysis of cyclohexanone. Aldehyde was not observed, whereas major products were hydrocarbons; (b) D. C. Montague and F. S. Rowland, *J. Amer.*

implication that k_{ISC} and k_{IC} (if any) are competitive with the collisional relaxation at $\sim$100 Torr of added gas ($\omega \sim 10^9$ sec^{-1}) is reasonable, since the fluoresence decay time (τ_F) of S_1^* is estimated as 10^{-9} to $\sim 10^{-8}$ sec, invariant over the entire $S_0 \rightarrow S_1$ absorption band (320–250 nm) in the gas pressure region of concern here.[25] (7) The intermediate Y can cyclize, before its decomposition, to give cyclohexanone back, with the possibility of geometric isomerization, if *cis* or *trans* 2,6-disubstituted cyclohexanone is used.[13]

There are some minor features which are left out. For example, it is not possible to rule out that the intermediate Y directly decomposes to the hydrocarbon products without going through the intermediate Z at low excitation energy. The fact that the 5-hexenal quantum yield at 313 nm is 0.16 in the gas phase and 0.11 in 3-methylpentane solution or 0.27 in pure liquid[11] suggests that the missing quantum yield can be as much as 0.8 in the low-energy photolysis, but it is difficult to assess the importance of the internal conversion yield without performing photolysis at very low pressures. Yet, it is difficult to rule out the *hot* ground-state cyclohexanone as an intermediate which contributes partially to the yields of 1-pentene and cyclopentane.

A recent report of the direct potolysis of cyclohexanone in solution shows that the photoisomerization to 5-hexenal involves a triplet precursor; the aldehyde yield is quenched by 1,3-pentadiene and isopropyl alcohol.[26] Therefore, the present mechanism involving a triplet intermediate in the gas phase is consistent with the triplet mechanism postulated in solution.

General Mechanistic Considerations

The structural distinction between intermediates X and Y is worthy of some speculation, since no direct structural evidence is available. Since both geometric isomers (*cis* and *trans*) of the 5-heptenal are produced in the photolysis of 2-methylcyclohexanone,[13] the precursor must be capable of giving the *trans* and *cis* aldehydes. Thus, one can consider it to be a seven-membered cyclic oxycarbene intermediate as shown in Figure 8. There are two conformations of this intermediate (X_a' and X_b'), from which one 5-heptenal isomer (*cis* or *trans*) each can be derived, when the carbene at C_1 abstracts the H atom at C_5 and the C_6–O_7 bond cleaves in a concerted manner. Clearly, these seven-membered cyclic oxycarbenes (X_a' and X_b') may be formed from the T_1 state of 2-methylcyclohexanone (X). The rate of formation of the intermediate Y (a diradical formed by the cleavage of the C_1–C_6 bond in cyclohexanone) is likely to be favored over the rate of formation of the cyclic intermediate X_a' or X_b' at higher excitation energy, and this would be consistent with the observation that the HA/C5 ratio decreases with the shortening of the photolysis wavelength. It is also convenient to note a probable structural distinction between the intermediate X (T_1) and its daughter intermediate X_a' or X_b'; the X is most likely to resemble the geometry of cyclohexanone but with a radical center at the O atom, since cyclohexanol was observed in the photolysis of cyclohexanone in 2-propanol.[26] It should be stated that an intermediate like X_a' or X_b' is not likely to yield, in a concerted manner, *cis*- and *trans*-2-6-dimethylcyclohexanone,[13] and therefore the intermediate Y probably gives rise to these isomers.

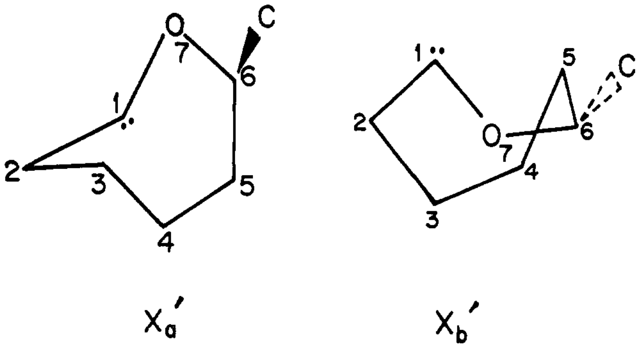

Figure 8. Seven-membered cyclic oxycarbene intermediates.

A somewhat different intermediate for the formation of the 5-heptenals has been proposed earlier.[13] Furthermore, cyclic oxycarbene intermediates have been invoked in the photolysis of camphor and cyclobutanones[27] in the liquid phase, whereas no cyclic acetal formation through such an intermediate has been observed in cyclopentanone.[27b,28] Therefore, the intermediacy of X_a' and X_b' is only speculative.

It is interesting to note that the product distribution obtained at 0.1 Torr of cyclohexanone in benzene-sensitized runs where the triplet sensitization predominates (see Tables V and VI) is similar to the distribution obtained at 313 nm where 1.0 Torr of cyclohexanone is directly photolyzed (see Tables I and II). A probable reason for this similarity lies in the fact that the $S_1 \rightsquigarrow T_1$ intersystem crossing following the direct excitation is extremely efficient (quantum yield of near unity)[25] compared with other unimolecular processes, and that, in both cases, the energetics are similar. Naturally, it is expected that the triplet mercury ($^3P_1$) sensitization is likely to give a product distribution similar to that obtained at 270 nm[24b] by direct photolysis, if the $S_1 \rightsquigarrow T_1$ intersystem crossing predominates over others. Therefore, it is not too surprising to find that the sensitized product distributions simply reflect the excitation energy variation from the intermolecular transfer, in agreement with the suggestion made by Badcock, *et al.*[13a] Therefore, in the case of cyclohexanone, it is still conceivable that the reactivities of the S_1 and T_1 are very different but that we are unable to sample the true chemical reactivity of S_1 except for its ability to intersystem cross by a radiationless transition ($S_1 \rightsquigarrow T_1$).

Energy Transfer Cross Sections

The singlet energy transfer from benzene to cyclohexanone has a $\pi\sigma^2$ cross section of $\sim$55 Å^2, if a value of 60 ± 20 nsec[29a] for the $^1B_{2u}$ benzene lifetime and a value of 2.5 Torr of cyclohexanone for $P_{1/2}$ are used. If a value of 2.92 Torr of cyclohexanone obtained from the fluorescence quenching experiment[19] is used instead,

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Chem. Soc., **91**, 7230 (1969). About 105 kcal/mol is transferred to cyclobutanone from the triplet mercury.

(25) R. G. Shortridge, Jr., C. F. Rusbult, and E. K. C. Lee, the preliminary result of a fluorescence excitation spectroscopy done at extremely low luminosity, manuscript in preparation.

(26) R. Simonaitis, G. W. Cowell, and J. N. Pitts, Jr., *Tetrahedron Lett.*, 3751 (1967).

(27) (a) W. C. Agosta and D. K. Herron, *J. Amer. Chem. Soc.*, **90**, 7025 (1968); (b) N. J. Turro and R. M. Southam, *Tetrahedron Lett.*, 545 (1967).

(28) P. Yates, *Pure Appl. Chem.*, **16**, 93 (1968).

(29) (a) G. M. Breuer and E. K. C. Lee, *J. Chem. Phys.*, **51**, 3130 (1969); (b) T. Chen and E. W. Schlag in "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, Inc., New York, N. Y., 1969, p 381.

then a $\pi\sigma^2$ quenching cross section of 47 Å^2 is obtained, in reasonable agreement with the value obtained by the chemical product analysis. The singlet energy-transfer cross section from benzene to cyclohexanone is nearly equal to those obtained earlier for the benzene–cyclobutanone[3] and benzene–cyclopentanone[4] systems, provided that they are evaluated on the basis of the newly obtained value of the $^1B_{2u}$ lifetime.[19,29] It is apparent that, on the average, the singlet energy transfer takes place in every other collision.

The triplet energy transfer from benzene to cyclohexanone has a cross section of $\sim$1.3 Å^2, if a triplet lifetime value of 70 μsec[30] for the $^3B_{1u}$ benzene and a $P_{1/2}$ value of 0.09 Torr of cyclohexanone are used. Again, the triplet-quenching cross sections obtained for cyclohexanone, cyclobutanone,[3] and cyclopentanone[4] are alike within the accuracy of the measurement. The smallness of these triplet-quenching cross sections is understandable in terms of the rate–energetics correlation,[31] since the triplet energies of these ketones are likely to be 75–80 kcal/mol as compared to 84 kcal/mol for benzene.

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(30) (a) C. S. Parmenter and B. L. Ring, *J. Chem. Phys.*, **46**, 1998 (1967); (b) see footnote 23 of ref 3.

(31) (a) R. E. Rebbert and P. Ausloos, *J. Amer. Chem. Soc.*, **87**, 5569 (1965); (b) M. W. Schmidt and E. K. C. Lee, *ibid.*, **90**, 5919 (1968).

Reevaluation of the Formation Constants of the Hydrated Proton in Acetonitrile[1]

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Abstract: Values of the hydration constants $K^f_{H^+{}_{nw}}$ of the proton in acetonitrile (AN), calculated previously[2] from spectrophotometric measurements of the activity of the solvated proton, $a_{H_s^+}$ in dilute perchloric acid solutions in the presence of water, using *o*-nitro-, *m*-nitro-, *o*-nitro-*p*-chloroaniline, and dibromothymolbenzein as indicators, are somewhat in error because the calculations were based on the incorrect assumption that the monoprotonated acid forms, BH^+, of these bases are not being hydrated under the experimental conditions. In the present paper it is found that BH^+ forms a mono- and a dihydrate. The following values for the formation constants $K^f_{BH_w{}^+}$ and $K^f_{BH_{2w}{}^+}$ were found: *m*-nitroanilinium, 1.0, 5.2; 2-nitro-4,5-dimethylanilinium, 0, 1.2 × 10; anilinium, 0.8, 1.8; and *p*-naphtholbenzeinium, 2.1 and 4.3, respectively. $pK^d_{BH^+}$ of 2-nitro-4,5-dimethylaniline was found to be 5.66. From infrared and, in some instances, from potentiometric p*a*H measurements it is found that the above bases B in the uncharged form are not hydrated in AN up to a water concentration of 1.5 *M*. Using the above hydration constants, values of $K^f_{H^+{}_{nw}}$ have been recalculated. The hydration constants of the proton were also obtained from conductivity data and from spectrophotometrically determined paH_s values in poorly buffered picric acid solutions containing water, using *p*-naphtholbenzein as indicator. Hydration of the protonated indicator base was taken into account. In general, agreement between the *y* values (eq 5) and hence between the hydration constants of the proton from the perchloric and picric acid data is satisfactory. Values of the overall proton hydration constants are $K^f_{H_w{}^+} = 1.6 \times 10^2$, $K^f_{H_{2w}{}^+} = 8 \times 10^3$, $K^f_{H_{3w}{}^+} = 6 \times 10^4$, and $K^f_{H_{4w}{}^+} = 2 \times 10^5$. When the water concentration is 1 *M*, about 80% of the protons are in the form of tetrahydrate.

In a previous paper[2] data were presented on the hydration of the solvated proton, H_s^+, in acetonitrile (AN) and values of the formation constants $K^f_{H_{nw}{}^+}$ were calculated. Hammett indicators were used to determine $[H^+]_s$ in dilute perchloric acid solutions in AN in the presence of water. Evidence was presented that the indicators used, *o*-nitro- and *o*-nitro-*p*-chloroaniline, are not hydrated in AN when the water concentration is <1 *M*. This is verified in the present study from the spectrum of the first overtone of the –OH stretch of free water at 1410 mμ in AN in the presence of the bases *o*- and *m*-nitroaniline, and also of aniline. It is assumed, as it was by Coetzee,[3] that the hydrogen-bonded H···NH band does not overlap with that of the free –OH band. Inconclusive evidence was presented in a previous study that the monoprotonated forms IH^+ of the indicators (I) used are not hydrated. From the spectrophotometric determination in AN of the overall dissociation constant of picric acid in the presence of water[4] strong indication was obtained that in perchloric acid–water mixtures the reported values of y^2 in the equation $[H^+]_s = C_{HClO_4}/y$ are too small. The most plausible explanation for the deviation is that the protonated forms of the uncharged indicator bases used are being hydrated. In the present paper the hydration of IH^+ was calculated from the effect of water on the potentiometric determined values of paH_s with the glass electrode in buffered mixtures of perchloric acid containing an excess of 2-nitro-4,5-dimethyl- or *m*-nitroaniline. Results are also presented with aniline. These bases are sufficiently strong such that when $C_{H_2O} \leqq 0.5$, $\Sigma[H^+] = [H^+]_s + \sum_{n=1}^{n=4} [H^+]_{nw}$

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