Intermolecular Triplet Energy Transfer. III. From Benzene to 2-Chlorocyclobutanone and the Trans and Cis Isomers of 2,3- and 2,4-Dimethylcyclobutanones[1]

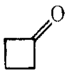
John Metcalfe and Edward K. C. Lee*

Contribution from the Department of Chemistry,
University of California, Irvine, California 92664. *Received October 10, 1972*

Abstract: The triplet energy transfer rates from C_6H_6 ($^3B_{1u}$, 84.4 kcal/mol) to cyclobutanone (CB), chlorocyclobutanone (Chloro CB), and the cis and trans isomers of 2,3- and 2,4-dimethylcyclobutanones (DMCB) have been measured in the gas phase. These ketones have their triplet energies (E_T) below 84 kcal/mol. The collisional electronic quenching efficiencies range from 0.01 for CB to 0.4 for Chloro CB, and an explanation for the quenching based on the exchange mechanism is given. The degree of the substituent effect on the $\sigma_Q{}^2$(triplet) by α-CH_3 substitution ($2\times/CH_3$) is much less than α-Cl substitution on the $\sigma_Q{}^2$(triplet). This positive α-CH_3-substituent effect on the $\sigma_Q{}^2$(triplet) cannot be due to "steric hindrance" which seems to operate on the $\sigma_Q{}^2$(singlet).

The mechanism and rates of the intermolecular triplet electronic energy transfer processes involving the benzene ($^3B_{1u}$, 84.4 kcal/mol) donor and a variety of simple π-bonded acceptor molecules in the gas phase have been studied extensively in the past 10 years.[2-6] The triplet energy transfer process can be used to evaluate the yield of the aromatic triplet state either by the sensitized phosphorescence emission from biacetyl[2] or by the sensitized cis–trans isomerization of a 2-butene isomer[3] and critical reviews on this subject are available in literature.[7] A review dealing with the application of these methods and the singlet benzene ($^1B_{2u}$, 109 kcal/mol) sensitization to the kinetic studies of the photochemistry of carbonyl compounds is also available.[8]

The present study is a brief extension of our earlier systematic study on the rates and mechanisms of the intermolecular triplet energy transfer in the gas phase,[5,9] and it specifically examines the effects of the α-chlorine substitution **2** and the α-methyl substitutions **3–6** on the cyclobutanone ring **1**. Furthermore, the α-substituent effects observed in the triplet benzene sensitization of these cyclobutanones here will be compared with the steric hindrance (due to α-methyl substitutions) observed in the singlet benzene sensitization of aliphatic ketones.[10]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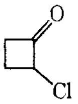
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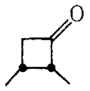
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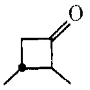
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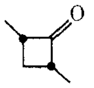
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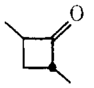
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Experimental Section

Cyclobutanone (Aldrich Chemical Co.) was used after degassing *in vacuo* at liquid nitrogen temperature, since it was of sufficient purity (>99%) for this study. Chlorocyclobutanone (**2**) was prepared by the method used by Durig and Green[11] and purifed by vpc as described in detail elsewhere.[12] The four isomers of dimethylcyclobutanones (**3–6**) were prepared and purified in the manner described earlier.[13] Zone-refined grade benzene (Litton Chemicals, >99.999%) and *cis*-2-butene (Phillips Research grade, >99.9%) were used after degassing *in vacuo* at liquid nitrogen temperature.

Samples were handled on a glass–metal vacuum line free from grease and mercury, and photolysis mixtures were contained in a quartz cylindrical cell of 5.0-cm od and 5.0-cm length. Irradiation of the samples was at 253.7 nm, using a low-pressure mercury grid lamp (Mineralight R51, Ultraviolet Products, Inc.) with a Corning CS-7-54 filter and a 1.0 cm thick D_3P filter solution as described elsewhere.[14] The product separation by vpc was carried out on a DMS column (30%, 0.25-in. o.d. by 25 ft, 23°) for the hydrocarbone (C_2, C_3, and C_5's from **1** and **3–6**)[13] or on a Carbowax-300 column (20%, 0.25-in. o.d. by 25 ft, 23°) for the chlorohydrocarbons (C_2 and C_3's from **2**).[12] The product yields were determined with a hydrogen flame ionization detector (Perkin-Elmer, F-11) and a 1-mV potentiometer recorder with a Disc integrator.

Results

The following mechanism should be considered for the competitive quenching of the triplet benzene ($^3C_6H_6$ or $^3B_{1u}$) by *cis*-2-butene and the substituted cyclobutanones (XCB).

$$\text{unimolecular decay: } {}^3C_6H_6 \longrightarrow C_6H_6 \qquad (1)$$

$$\text{self-quenching: } {}^3C_6H_6 + C_6H_6 \longrightarrow 2C_6H_6 \qquad (2)$$

$$\text{butene-quenching: } {}^3C_6H_6 + cis\text{-B} \longrightarrow C_6H_6 + {}^3(cis\text{-B}) \qquad (3)$$

$$\text{XCB-quenching: } {}^3C_6H_6 + \text{XCB} \longrightarrow C_6H_6 + {}^3(\text{XCB}) \qquad (4)$$

$$\text{isomerization: } {}^3(cis\text{-B}) \begin{cases} \longrightarrow trans\text{-2-butene} & (5t) \\ \longrightarrow cis\text{-2-butene} & (5c) \end{cases}$$

$$\text{decarbonylation: } {}^3(\text{XCB}) \longrightarrow \text{X-cyclopropane} + \text{CO} \qquad (6)$$

It has been shown[8,15] that a steady-state kinetic

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(1) Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for the financial support of this research.

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(11) J. R. Durig and W. H. Green, *J. Mol. Spectrosc.*, **27**, 95 (1968).

(12) J. Metcalfe and E. K. C. Lee, a pyrolysis paper on **2** to be published.

(13) H. A. J. Carless, J. Metcalfe, and E. K. C. Lee, *J. Amer. Chem. Soc.*, **94**, 7221 (1972).

(14) R. G. Shortridge, Jr., and E. K. C. Lee, *ibid.*, **92**, 2228 (1970).

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Table I. Triplet Benzene ($^3B_{1u}$) Half-Quenching Pressures of *cis*-2-Butene ($P_{1/2}$) for a Given Value of the Competing Quencher Pressure (P_Q; Q = XCB), Quenching Rate Coefficient (k_Q), Quenching Cross Sections (σ_Q^2), and On-Set of the $^1(\pi^* \leftarrow n)$ Absorption Wavelength (λ_i)

Quencher	P_Q, Torr	$P_{1/2}$, Torr	$P_{1/2}/P_Q$	k_Q, 10^{10} M^{-1} sec^{-1}	σ_Q^2, Å^2	λ_i, nm[a]
CB	0.20	0.065	0.32	0.19 ± 0.03	0.25	~324
cis-2,3-DMCB	0.20	0.13	0.65	0.54 ± 0.07	0.77	328
trans-2,3-DMCB	0.20	0.11	0.55	0.45 ± 0.07	0.64	328
cis-2,4-DMCB	0.20	0.16	0.80	0.67 ± 0.08	0.96	327
trans-2,4-DMCB	0.20	0.22	1.10	0.97 ± 0.10	1.40	331
Chloro CB	0.050	0.42	8.4	7.9 ± 0.8	11.6	341

[a] λ_i value was arbitrarily chosen to be the value of absorption wavelength where the molar absorptivity (ϵ) is 10% of the ϵ_{max} value of the ketone.[18, 19]

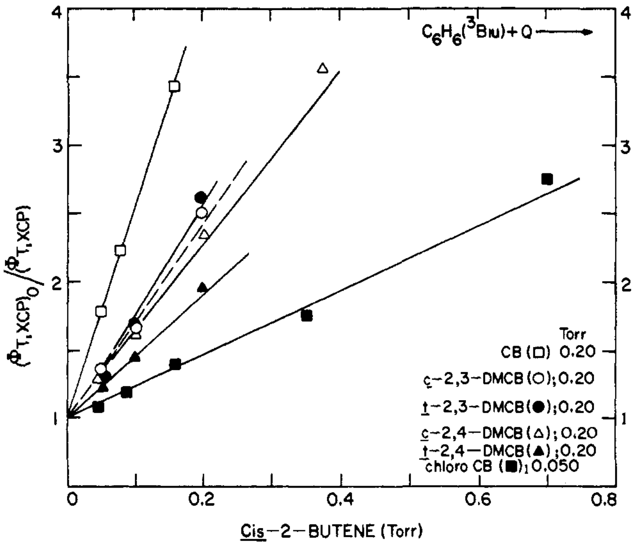

Figure 1. Stern–Volmer plots for competitive quenching of C_6H_6 ($^3B_{1u}$) by *cis*-2-butene in the presence of various cyclobutanones (see eq 7).

treatment gives a simple Stern–Volmer equation, if the change in the decarbonylation product is measured as a function of the *cis*-2-butene pressure variation while the C_6H_6 and CB pressures are kept constant

$$\frac{[\Phi_{T,XCP}]_0}{[\Phi_{TX,CP}]} = 1 + \frac{k_3(cis\text{-B})}{\{k_1 + k_2(C_6H_6) + k_4(XCB)\}} \quad (7)$$

where $[\Phi_{T,XCP}]_0$ and $[\Phi_{T,XCP}]$ are the quantum yield of decarbonylated cyclopropane products resulting from eq 6 in the absence and in the presence of *cis*-2-butene, respectively. The use of this expression does not require the measurement of the isomerization yield from *cis*-2-butene and also avoids the kinetic complication which might arise when the excited singlet benzene ($^1B_{2u}$) is quenched by the ketones. At the half-quenching pressure of *cis*-2-butene for the decarbonylation product (XCB), $P_{1/2}(cis\text{-B}; XCB)$, $k_3(cis\text{-B})_{1/2} = k_1 + k_2(C_6H_6) + k_4(XCB)$. Since $k_1 + k_2(C_6H_6)$ is known to be 1.43×10^4 sec^{-1} at 2.5 Torr of benzene pressure[16] and $k_3 = 1.0 \times 10^{10}$ M^{-1} sec^{-1},[5,8,17] we could obtain eq 8 if k_Q is expressed in the unit of M^{-1} sec^{-1} where 1 Torr is equal to 5.43×10^{-5} M at 23°.

The decarbonylation products arising from the $C_6H_6(^3B_{1u})$ sensitization of the DMCB isomers (**3**–**6**) are *cis*- and *trans*-dimethylcyclopropanes (DMCP, **7** and **8**, respectively),[13] whereas the corresponding "primary" product from Chloro CB (**2**)[18] is chlorocyclopropane (Chloro CP, **9**) which is *vibrationally hot.*

$$k_Q = k_4 = \frac{k_3(cis\text{-B})_{1/2} - [k_1 + k_2(C_6H_6)]}{(XCB)} = \frac{1.0 \times 10^{10}(cis\text{-B})_{1/2} - 1.43 \times 10^4 \text{ sec}^{-1}}{(XCB)} \quad (8)$$


7


8

9

Some unimolecular decomposition products from this vibrationally hot Chloro CP are formed at low pressures (≤2.55 Torr of total pressure): 3-chloropropene (≤15%), *cis*- and *trans*-1-chloropropene (≤0.8%), and methylacetylene and allene (≤0.8%) which were produced by HCl elimination.[12]

The CB (**1**) and DMCB (**3**–**6**) pressures were fixed at 0.20 Torr while the Chloro CB (**2**) was fixed at 0.050 Torr at 23°. Stern–Volmer plots fitting eq 7 are shown in Figure 1. Quenching rate coefficient and cross sections are tabulated in Table I. Since the electronic origins of the $S_1 \leftarrow S_0$ ($\pi^* \leftarrow n$) transition,[19] "0–0" band, are not accurately known, we have chosen the on-set wavelengths of absorption (λ_i) as those defined in the footnote *a* of Table I.

Discussion

The redetermined value of k_Q for CB (**1**) here is ~25% lower than the previously determined value,[15] but they agree within the limits of experimental errors involved. If we take the average of the two values, then we obtain $(k_Q)_{CB} = 0.22 \times 10^{10}$ M^{-1} sec^{-1} for CB (**1**). The average values of cis and trans isomers are $(k_Q)_{2,3} = 0.50 \times 10^{10}$ M^{-1} sec^{-1} for the 2,3-DMCB (**3** and **4**) and $(k_Q)_{2,4} = 0.82 \times 10^{10}$ M^{-1} sec^{-1} for the 2,4-DMCB isomers (**5** and **6**). This incremental increase by a factor of ~2 for each α-CH_3 substitution (α-position to C=O group) on the cyclobutanone ring is similar in magnitude to that observed for each CH_3 substitution on the vinylogous position of C_2H_4.[5,6,8] It should however be recognized that in the case of ethylenes, $^3(\pi \leftarrow\!\!\sim\!\!\sim \pi)$, the CH_3 group is on the carbon atoms with the π^* orbital whereas in the case of CB's, $^3(\pi^* \leftarrow\!\!\sim\!\!\sim n)$, the CH_3 group is one carbon removed from the carbon atom with the π^* orbital.

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[16] (a) C. S. Parmenter and B. L. Ring, *J. Chem. Phys.*, **46**, 1998 (1967); (b) see footnote 23 of ref 15.

[17] C. S. Burton and H. E. Hunziker, *Chem. Phys. Lett.*, **6**, 352 (1970).

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[19] (a) J. C. Hemminger and E. K. C. Lee, *J. Chem. Phys.*, **56**, 5284 (1972); (b) J. C. Hemminger, H. A. J. Carless, and E. K. C. Lee, a paper on the laser-excited fluorescence emission from the DMCB isomers: *J. Amer. Chem. Soc.*, **95**, 682 (1973).

It is interesting to note that each α-CH_3 substitution on the cyclobutanone ring increases $\sim$2 times the σ_Q^2 value for the $^3(\pi^* \leftsquigarrow n)$ transition, caused by energy transfer from $C_6H_6(^3B_{1u})$, relative to that for CB (triplet energy transfer probability of 0.01/collision), whereas no such increase on the σ_Q^2 values for the $^1(\pi^* \leftsquigarrow n)$ transition, caused by energy transfer from $C_6H_6(^1B_{2u})$, is observed.[20]

The σ^2 values for $^1(\pi^* \leftsquigarrow n)$ by energy transfer from $C_6H_6(^1B_{2u})$ to CH_3-substituted acetones show instead substantial reduction with increased CH_3 substitution,[10,21] and this observation has been explained on the basis of steric hindrance.[10] The true origin of this steric hindrance can be easily rationalized on the basis of the model for the gas-phase singlet energy transfer mechanism involving the combination of the Dexter type ("short range" exchange) and the Förster type ("long range" dipole–dipole) interactions between the singlet aromatic excitation donor ($^1D^*$) and the carbonyl acceptor (A).[22] With the $C_6H_6(^1B_{2u})$ as $^1D^*$, the exchange mechanism contributes more than the dipole–dipole mechanism to the electronic quenching,[22] and hence the steric hindrance for the short-range interaction between $^1D^*$ and A plays an important role.

The origin of the CH_3-group enhanced and *particularly* Cl-atom (α-substitution) enhanced triplet energy transfer rates, $^3(\pi^* \leftsquigarrow n)$, may lie with the operation of the exchange mechanism (Dexter type),[9,23] since these substituent groups could *enhance* the spectral overlap of the donor deexcitation ($T_1 \rightarrow S_0$) with the acceptor excitation ($T_1 \leftarrow S_0$) by lowering the triplet energies of the acceptor upon α-substitution.[9] The degree of the overlap can greatly be enhanced here, particularly, because the triplet energies (E_T) of $^3D^*$ and $^3A^*$ are very close to each other, *e.g.*, 84.4 and 80–84 kcal/mol, respectively.[24]

In the $C_6H_6(^1B_{2u})$/CB system, the spectral overlap is nearly complete and hence the singlet energy transfers efficiency is insensitive to the E_S values of ketones as expected.[22]

The extent of energy lowering of E_S (and probably E_T) in 2-chlorocyclobutanone (**2**) as compared with CB (**1**) by the chlorine atom substitution is quite substantial ($\leqslant 1500$ cm^{-1}) and it is surprising. Chloro CB (**2**) quenches $C_6H_6(^3B_{1u})$ with a collision efficiency of 0.3–0.4, comparable to 1,3-butadiene (E_T = 59.6 kcal/mol)[25] whose collision efficiency is $\sim$0.7.[8,9] It would be of interest to extend the present study to more highly substituted chlorocyclobutanones, and to compare the triplet energy transfer mechanism with the singlet energy transfer mechanism.

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(20) G. M. Breuer, Ph.D. Thesis, University of California, Irvine, 1972. In singlet benzene ($^1B_{2u}$) quenching in the gas phase, σ_Q^2 for CB, *cis*-2,4-DMCB, *trans*-2,4-DMCB, cyclopentanone (CP), and *trans*-2,5-DMCP are insensitive to the α-methyl substitutions and are 25, 27, 24, 24, and 25 Å^2, respectively.

(21) σ_Q^2 for acetone, 3-pentanone, 2,4-dimethyl-3-pentanone, and 2,2,4,4-tetramethyl-3-pentanone are 10.4, 13.1, 8.9, and 3.0 Å^2, respectively.[10]

(22) G. M. Breuer and E. K. C. Lee, *Chem. Phys. Lett.*, **14**, 407 (1972).

(23) See for a review, A. A. Lamola in "Techniques of Organic Chemistry. XIV. Energy Transfer and Organic Photochemistry," P. A. Leermakers and A. Weissberger, Ed., Interscience, New York, N. Y., 1969, p 17.

(24) E_T of $C_6H_6(^3B_{1u})$ is 29,510 cm^{-1}. The first excited singlet energy (E_S) of cyclobutanone is 30,291.2 cm^{-1} (D. C. Moule, *Can. J. Phys.*, **47**, 1235 (1969)) and E_S of cyclopentanone is 30,514.0 cm^{-1} (H. E. Howard-Lock and G. W. King, *J. Mol. Spectrosc.*, **36**, 53 (1970)). Assuming an E_S–E_T splitting of 1000–1500 cm^{-1}, E_T for these unsubstituted cyclic ketones could be at 28,900–29,400 cm^{-1}.

(25) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

Localized Charge Distributions. V. Internal Rotation Barriers in Methylamine, Methyl Alcohol, Propene, and Acetaldehyde

Mark S. Gordon*[1a] **and Walter England**[1b]

Contribution from the Department of Chemistry, North Dakota State University,
Fargo, North Dakota 58102, and
Ames Laboratory—USAEC and the Department of Chemistry,
Iowa State University, Ames, Iowa 50010. *Received June 2, 1972*

Abstract: The internal rotation barriers of methylamine, methyl alcohol, propene, and acetaldehyde are investigated within the context of localized charge distributions defined in earlier papers. It is shown that, as for ethane, hydrogen peroxide, and borazane, the barriers can be understood in terms of changes in vicinal interference interactions within those orbitals adjacent to the axial bond. These vicinal interactions are compared with those in molecules studied previously. Such a comparison leads to a straightforward explanation of the observed trends in the barriers.

It has been demonstrated in earlier papers[2–4] that localized molecular orbitals (LMO's) are not generally completely localized on one or two atoms as in idealized valence-bond or lone-pair orbitals but rather have physically significant "tails" on atoms dihedrally displaced from the bond or lone pair. We have re-

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(1) (a) North Dakota State University. (b) Iowa State University.

(2) (a) Paper I: W. England and M. S. Gordon, *J. Amer. Chem. Soc.*, **93**, 4649 (1971); (b) Paper II: *ibid.*, **94**, 4818 (1972).

(3) Paper III: M. S. Gordon and W. England, *ibid.*, **94**, 5168 (1972).

(4) Paper IV: M. S. Gordon and W. England, *Chem. Phys. Lett.*, **15**, 59 (1972).