

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 87, NUMBER 20

OCTOBER 20, 1965

Physical and Inorganic Chemistry

The Roles of Molecular Structure and Environment in the Reactivity of Excited States¹

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The importance of molecular structure and environment in the reactivity of excited states was discussed and demonstrated by a study of two model photochemical systems in both conventional liquid medium and solid potassium bromide matrix. The two photochemical systems are the dimerization of anthracenes, which is a bimolecular reaction involving a π, π^ excited singlet and a ground-state monomer, and the cyclo-elimination process (type-II split) of butyrophenones, which is a unimolecular decomposition involving an n, π^* triplet state.*

Introduction

The reactivity of excited states in photochemical systems is often governed by factors such as molecular structure, nature of the environment, pressure, temperature, and excitation wave length. Detailed correlations between such parameters and the over-all photochemical reactivity require painstaking accumulation of quantitative experimental data; to date these are available only for a very few photochemical systems.

The photodimerization of anthracene and the photodecomposition of butyrophenones in the condensed phase were chosen to study the roles of molecular structure and environment in the reactivity of the photochemical excited states. These two systems were chosen because they are quite different in the nature of reaction, the first one being a bimolecular reaction and the latter a unimolecular reaction. The condensed

phase was chosen as the reaction medium because an important simplification results. Since radiationless conversion to a Boltzmann equilibrium in the lowest excited singlet or triplet state usually occurs before any other processes, we can be fairly sure that we will be dealing with the same excited state in the condensed phase, whatever the wave length of excitation.

The photochemistry of anthracene in solution has been extensively studied and recently reviewed by Bowen.² It is now established that dimer formation involves a π, π^* excited singlet and a ground-state monomer. However, the photodimerization is markedly influenced by *meso* substitution. Thus, substitution in both the 9- and 10- *meso* positions in anthracene prevents the formation of stable dimers,^{3a} whereas substitution at only one of the *meso* positions with an alkyl^{3a} or aldehyde^{3b} group gives stable dimers, but with a lower quantum yield than for anthracene itself. Presumably the effect of *meso* substitution in the reduction of dimerization efficiency is largely due to steric hindrance.^{3a}

The photochemical decomposition of butyrophenone has been studied at 3130 Å. and at 25° in various solvents.⁴ The dominant reaction is the photocyclo-elimination of ethylene, commonly known as the type-II process. Recent e.p.r. and phosphorescence studies indicate that this type-II process involves an n, π^* triplet butyrophenone.⁵ The quantum yield of the

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(3) (a) J. B. Birks and J. B. Aladekomo, *J. Photochem. Photobiol.*, **2**, 415 (1963); (b) F. D. Greene, S. L. Misrock, and J. R. Wolfe, *J. Am. Chem. Soc.*, **77**, 3852 (1955); T. L. Brown, J. P. Kleiman, and S. T. Young, *Chem. Ind. (London)*, 850 (1959).

(4) J. N. Pitts, Jr., and E. J. Baum, to be published.

(5) E. J. Baum, J. K. S. Wan, and J. N. Pitts, Jr., Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p. 7S.

(1) Photochemical Studies in Alkali Halide Matrices. II. Presented at the Symposium on Structure and Photochemistry of Excited States, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

process is highly sensitive to the electron-donating power of the substituents. Thus, the quantum yields of ethylene formation for butyrophenone, *p*-methoxy-, and *p*-aminobutyrophenones are 0.40, 0.10, and 0.00, respectively. These relative reactivities correlate with those of substituted benzophenones with corresponding triplets in intermolecular H atom abstractions.^{6,7} Thus, one effect of the substituents is that of altering the nature of the lower excited states.

The effect of environment is studied by changing the reaction medium from a conventional liquid system to a solid potassium bromide matrix pressed at different pressures. The feasibility of qualitative and quantitative studies of solid-state chemical reactions including pyrolysis,⁸⁻¹⁰ photolysis,^{11,12} and radiolysis^{13,14} in pressed alkali halide disks of the type customarily used for infrared analysis has been amply demonstrated. The present research points out further that such a pellet technique would be a simple and convenient method for qualitative study of the chemical effect of pressure on solid reactions.

Experimental Section

Materials. Infrared spectroscopic grade potassium bromide powder supplied by Harshaw Chemical was dried overnight at 110°, immediately before use. Anthracene and 9-anthraldehyde were obtained from Matheson Coleman and Bell and were recrystallized from ethanol. *o*-Nitrobenzaldehyde was supplied by Aldrich Chemical and was used without further purification. Butyrophenone and its derivatives were supplied by Aldrich Chemical; the liquid compounds were purified by gas-liquid chromatography, whereas the solid butyrophenones were purified by recrystallization, sublimation, and zone refining techniques. All solvents used were of commercial spectroscopic grade.

Liquid Phase Photolysis. All solutions were vacuum degassed prior to irradiation in a quartz cell at room temperature. A PEK 100-w. high-pressure mercury arc with a suitable Jena interference filter (half-width 75 Å.) was used as light source. Lamp intensities were measured by the method of Parker and Hatchard.¹⁵ Reaction products were separated by conventional gas-liquid chromatography and identified by n.m.r., infrared, and mass spectroscopy.

Photochemical Study in KBr Matrix. Experimental details on the preparation of pellets have been given elsewhere.^{8,11} Pellets containing about 0.1 mole % of the organic materials in 500 mg. of KBr powder

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were prepared by pressing the mixtures in an evacuated die at 4, 6.7, and 10.6 kbars, respectively, for 12 min. The pellets were then removed from the press for ultraviolet irradiation while being suspended in the "analyzing" infrared beam of a Perkin-Elmer 221 infrared spectrophotometer. The ultraviolet source was a high-pressure mercury arc (Bausch and Lomb SP200) equipped with a Pyrex water filter cell and an interference filter system. Light intensities were measured by *o*-nitrobenzaldehyde actinometry,¹¹ which has been found to be independent of the pressure applied. The nature and the rates of the photochemical reactions were followed by recording the spectra as a function of time and the quantum yields of the reactions were determined.¹¹ For the photodimerization of anthracenes, the quantum yield of dimer formed was taken as one-half of the quantum yield of anthracenes disappeared. For anthracene the absorption band at 885 cm.⁻¹ was calibrated to follow its disappearance. Similarly, the absorption bands at 1240 and at 890 cm.⁻¹ were calibrated and used to follow the disappearance of 9-anthraldehyde and butyrophenone, respectively. Ultraviolet absorption spectra of the organic pellets were recorded on a Cary 14 spectrophotometer against a reference of pure KBr pellet.

Viscosity Measurements. The method of Bingham and Stephens¹⁶ and Lombardi¹⁷ was adapted to measure the high viscosities of the KBr pellets pressed at various pressures. The pellet, adhering firmly to its holder walls, was precisely seated into an aluminum cylinder. One end of the cylinder was open and attached to a pressure line. The other closed end was made flat to the pellet. A modified precision micrometer depth gauge was placed directly on top of the center of the pellet. If the thickness of the pellet *d* and the radius *r* of the pellet are known, then a known pressure *P* is applied to the open end for a measured amount of time *t*. The pellet will flow and the resulting deformation with height *h* is measured by the depth gauge. The viscosity η is then given by

$$\eta = Pr^2t/4hd$$

where η is in poises, *r*, *h*, and *d* are in cm., *t* is in seconds, and *P* is in dynes/cm.²

Results and Discussion

Photodimerization of Anthracene and of 9-Anthraldehyde. The maximum quantum yield of anthracene dimerization in oxygen-free solutions is about 0.3.² No precise quantum yield data on the dimerization of 9-anthraldehyde are available in the literature. In the solid phase at room temperature, pure anthracene gives a fluorescence quantum efficiency of 0.9.¹⁸ The photodimerization of either anthracene or 9-anthraldehyde in the solid state has not heretofore been reported.

When a typical KBr pellet containing 0.13 mole % of anthracene was exposed to light at 3650 Å., the infrared spectrum, observed during irradiation, gradually changed to one identical with the published dianthracene spectrum, as shown in Figure 1. Figure 2 shows the similar photoreaction of 9-anthraldehyde in a KBr

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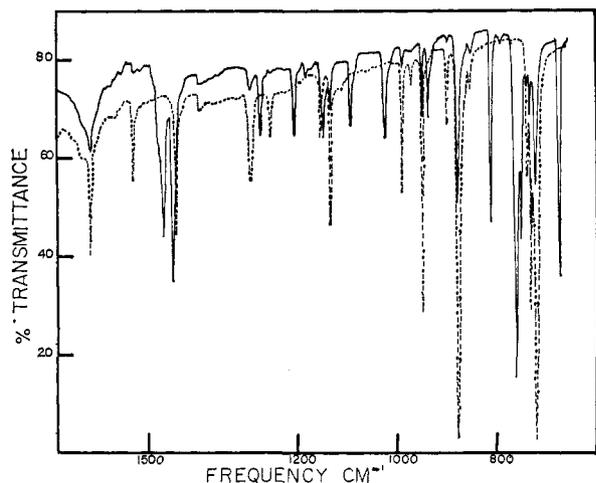


Figure 1. Spectra of the photodimerization of anthracene in a KBr pellet; dashed lines and solid lines correspond to *before* and *after* irradiation, respectively.

pellet; the carbonyl absorption band at 1665 cm^{-1} is shifted to 1720 cm^{-1} consistent with the attachment of the aldehyde groups in the dimer to sp^3 -hybridized saturated carbon atoms.

In two separate series of experiments with anthracene and with 9-anthraldehyde, the pressures at which the pellets were compressed were varied and the quantum yields of the dimerization were obtained as a function of pressure. The results are summarized in Table I where each of the values represents the average of 5 to 10 runs with deviations in the neighborhood of 5%. In Figure 3 the effect of pressure can best be presented by plotting $\log \Phi_P/\Phi_0$ against pressure, where Φ_0 is the extrapolated quantum yield at zero pressure.

Table I. Quantum Yields of the Dimerizations of Anthracene and 9-Anthraldehyde in a KBr Matrix at 3650 \AA . and at Various Pressures

System	Pressure, atm.	Φ^a
0.133 mole % anthracene	10,800	0.015
	6,800	0.018
	4,000	0.024
	0	0.039^b
0.114 mole % 9-anthraldehyde	10,800	0.13
	6,800	0.10
	4,000	0.08
	0	0.06^b

^a Represents an average of five to ten runs. ^b Obtained by extrapolation to zero pressure.

At this point it is necessary to consider how meaningful the pressure changes are and what the state of aggregation of the organic compounds is in the potassium bromide matrix at various pressures. First, we assume that the pressure applied to the pellet in the die is hydrostatic in nature. During compression, the exact pressure in the pellet would probably be very close to the hydrostatic pressure applied, since alkali halide powders have been found to be excellent pressure transmitters.¹⁹ After the pellet is removed from the press, there is no simple way in our experimental setup to measure the exact pressure within the pellet and

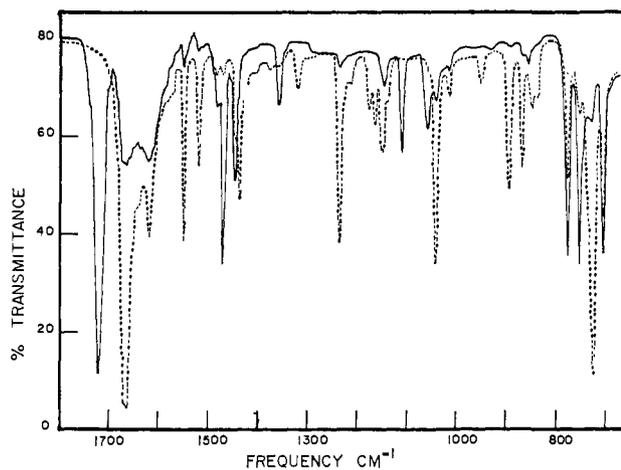


Figure 2. Spectra of the photodimerization of 9-anthraldehyde in a KBr pellet; dashed lines and solid lines correspond to *before* and *after* irradiation, respectively.

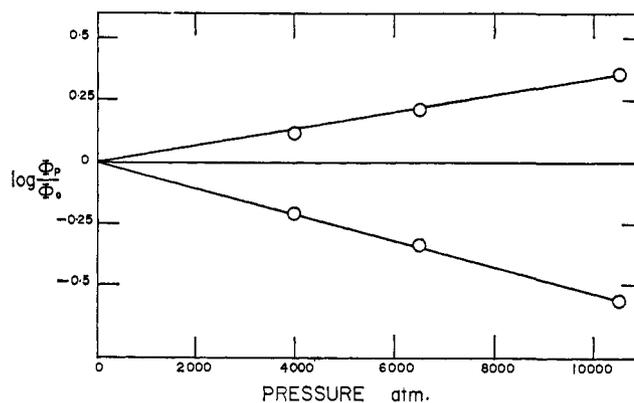


Figure 3. The effect of pressure on the quantum yields of photodimerizations; upper curve for 9-anthraldehyde and lower curve for anthracene.

whether it is changing with time. However, from a series of viscosity measurements, the results of which are in Table II, it is assumed that the high internal pres-

Table II. Viscosity Measurements of KBr Pellets at Various Pressures

System	Applied pressure, atm.	Viscosity, poise
Pure KBr	10,800	1.29×10^{14}
	6,800	0.69×10^{14}
	4,000	0.38×10^{14}
0.133 mole % anthracene in KBr	10,800	0.22×10^{14}
	6,800	0.14×10^{14}
	4,000	0.08×10^{14}
0.114 mole % 9-anthraldehyde in KBr	10,800	0.13×10^{14}
	6,800	0.09×10^{14}
	4,000	0.05×10^{14}

sure in the pellet can be supported owing to the high viscosity of the matrix.¹⁹ Since the pellet viscosities shown in Table II appear to be a direct function of the compressing pressure in the experimental range, it would be reasonable to postulate that the internal pres-

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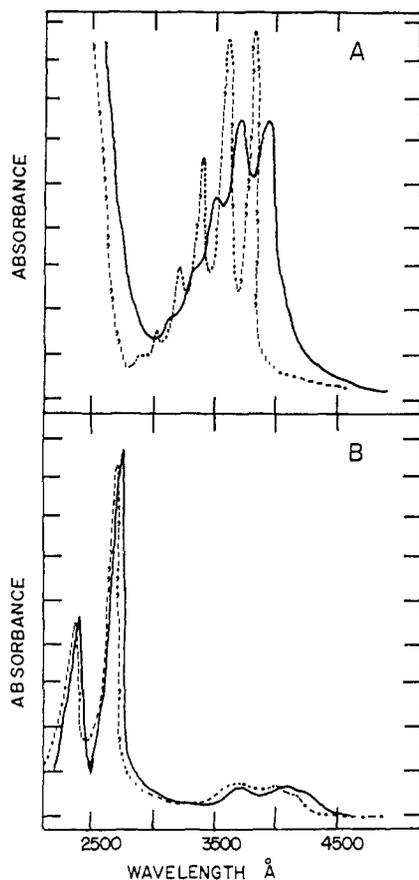


Figure 4. Ultraviolet absorption spectra of anthracene (A) and 9-anthraldehyde (B) in cyclohexane (dashed lines) and in KBr matrix (solid lines).

sure of the pellet, although not measurable, is also a direct function of the corresponding applied pressure. Thus, it seems that such a "pellet" technique would be a simple and convenient method for qualitative study of the effect of pressure on solid chemical reactions.

We will consider next the state of aggregation of the organic material in the KBr pellets with respect to the variation of pressure. In Figure 4 the near-ultraviolet absorption spectra of anthracene and 9-anthraldehyde pressed in KBr disks at 6800 atm. are given along with their corresponding spectra in cyclohexane solutions. The concentrations of the organic materials were reduced 100-fold from the 0.13 mole % in order to obtain better spectra, since the original concentration used in photochemical experiments was chosen to give complete absorption of the 3650-Å. line. Except for a red shift of the absorption peaks accompanied by broadening, the pellet spectra were similar to the respective solution spectra. These observations are in good accord with those reported by Wiederhorn and Drickamer,²⁰ who studied the optical absorption characteristics of anthracene and other fused ring aromatic hydrocarbons in alkali halide matrix under ultrahigh pressures and attributed the red shift and broadening largely to increase in dipole-dipole interaction. In Figure 5 the ultraviolet absorption spectra of the KBr pellets of anthracene and 9-anthraldehyde, after 5 hr. of irradiation, are shown together with the ultraviolet absorption spectrum of a pure KBr pellet.

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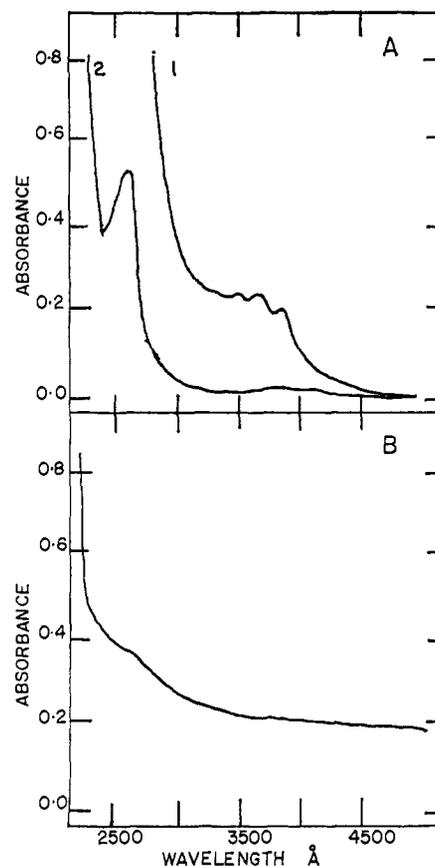


Figure 5. Ultraviolet absorption spectra of KBr-anthracene (curve 1, A) and KBr-9-anthraldehyde (curve 2, A) after 5-hr. irradiation, and of pure KBr pellet (B).

Thus, it is seen from both ultraviolet and infrared measurements that the organic materials did not chemically interact with the KBr matrix. In addition, orienting various portions of pellets of different pressures in the ultraviolet and infrared analyzing beams did not change the amount of absorption. This suggests that the organic material may be uniformly dispersed in the matrix independent of pressure within the experimental range.

We will now consider the pressure effect on the quantum efficiencies of the dimerizations. We have seen that the pressure changes the macroscopic viscosities of the pellets and that in most bimolecular reactions diffusion plays an important role. Thus, the pressure effect could simply be a diffusion effect. However, the following considerations tend to indicate that dimerization takes place between nearest neighbors and the viscosity is not a major controlling factor.

Although the macroscopic viscosities of the pellets are at least several orders of magnitude higher than those of a conventional liquid system, the quantum yield of dianthracene formation in the pellets is only about 100-fold smaller. Furthermore, since both anthracene and 9-anthraldehyde dimerizations are bimolecular, variation in viscosity due to pressure should have the same effect on both reactions. By the same argument, if the pressure effect is attributed largely to the dependence of distribution of organic aggregates in the pellets, the effect should be in the same direction for both dimerizations. However, the experimental findings show that an increase in pressure has opposite effects on the

dimerizations of anthracene and 9-anthraldehyde, the former being decreased by pressure and the latter increased.

Thus, we assume that the pressure effect on the quantum yields of dimerization is determined by the molecular expansion or contraction that is needed to form the transition state, according to the equation $\partial \ln k / \partial P = -\Delta V^* / RT$, where k is the rate constant of the photodimerization. At constant light intensity and identical initial anthracene concentration, Φ becomes directly proportional to k . It follows from the results that ΔV^* is about 2.8 ml. mole⁻¹ for the dimerization of anthracene, and about -2.0 ml. mole⁻¹ for 9-anthraldehyde. In the case of anthracene, there is no steric hindrance at the ends of the interacting dipoles responsible for dimerization. However, it is well established^{21,22} that in dianthracene the central rings are nonplanar and the outer benzene rings are bent out from the original molecular plane. Thus, it is perhaps not too difficult to imagine that the transition-state configuration could have a greater volume than the reactants. On the other hand, quantum yields of dimerization of 9-substituted anthracenes in solution have been found to be less than that of anthracene, probably owing to steric hindrance by the 9-substituent.^{3a} For 9-anthraldehyde Jones²³ has estimated from molecular models that in the ground state the aldehyde group is twisted by a minimum of about 45° relative to the anthracene nucleus. However, Hamilton²⁴ has shown for 9,10-diphenylanthracene that the excited state has a 10% smaller angle of twist than that of the ground state. If the excited state of 9-anthraldehyde also may have a smaller angle of twist than that of the ground state, the transition-state configuration would then have a smaller volume than the reactants. Furthermore, the observation and explanation of the pressure effect are in accord with the general prediction that the more sterically hindered a reaction is, the more it will be accelerated at high pressures.²⁵ Experiments are in progress in this laboratory to study the application of high pressure in bringing about the photodimerization of some 9,10-disubstituted anthracenes.

Photodecomposition of Butyrophenones. At room temperature and at 3130 Å., the major reaction of butyrophenone in oxygen-free solutions is the cyclo-elimination of ethylene (type-II split). The remaining fragment then quickly tautomerizes to acetophenone. The quantum yields of ethylene formation in the 3130-Å. photolysis of a series of butyrophenones in benzene solutions (0.1 M) are given in Table III. The quantum yields were found to be unchanged in other solvents, including cyclohexane, methylcyclohexane, cyclohexene, and isopropyl alcohol.

It is seen that substitution of electron-donating and -withdrawing groups on the phenyl ring markedly changes the reactivity of the butyrophenone toward photocycloelimination of ethylene. The effect is obviously different from that of the dimerization of anthracene, in which the effect of *meso* substitution is

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(22) J. B. Birks, J. H. Appleyard, and R. Pope, *J. Photochem. Photobiol.*, 2, 493 (1965).

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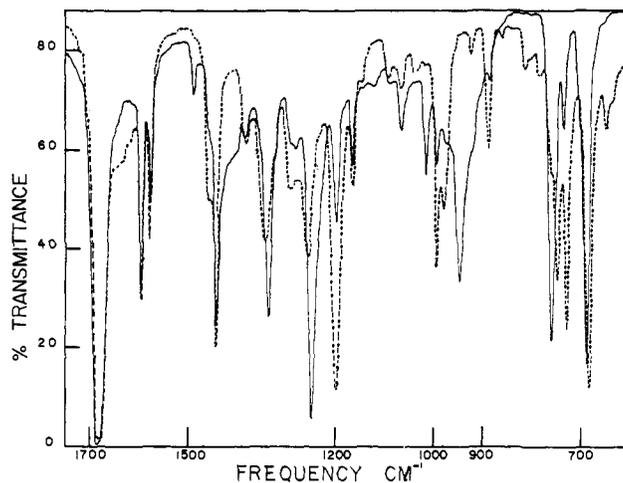


Figure 6. Spectra of the type-II process of butyrophenone in a KBr pellet; dashed lines and solid lines correspond to *before* and *after* irradiation, respectively.

mainly due to steric hindrance. Recent spectroscopic examination^{4,5} suggests that the lowest triplet state of these nonreactive *para*-substituted butyrophenones is π, π^* rather than n, π^* in character. Thus, the substitution effect is mainly due to a change of the electronic structure of the excited state and is an interesting illustration that different reactivity of excited states is influenced by their different electronic structure, even though they may have more or less the same energy.

Table III. Quantum Yields of Ethylene Formation in the 3130-Å. Photolysis of Butyrophenone Derivatives in Benzene Solution

Substituent	Φ
None	0.40
<i>p</i> -Methyl	0.39
<i>p</i> -Fluoro	0.29
<i>p</i> -Methoxy	0.10
<i>p</i> -Amino	0.00
<i>p</i> -Hydroxy	0.00
<i>o</i> -Hydroxy	0.00

The nature of the type-II split in butyrophenone was found not altered when the reaction was carried out in a KBr matrix. Figure 6 shows part of the infrared spectra of a potassium bromide-butyrophenone pellet before and after 6 hr. of irradiation at 3130 Å. The latter spectrum is identical with one of acetophenone except for bands at 1490 and 950 cm.⁻¹ which possibly may be due to ethylene trapped in the matrix. Therefore, it seems that the type-II split of butyrophenone requiring a six-membered cyclic intermediate occurs both in solution and in a solid matrix.

The state of aggregation of the butyrophenone in the KBr matrix is again difficult to define, especially since the butyrophenone is liquid at room temperature. It is likely that the liquid butyrophenone was adsorbed on KBr. When the mixture was pressed into pellet, butyrophenone molecules might be trapped evenly in the solid matrix. Table IV gives the ultraviolet absorption characteristics of some butyrophenones both in cyclohexane solution and in KBr matrix. The $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions are assigned conventionally. It is seen in the KBr matrix, the π, π^* bands

Table IV. Electronic Spectral Characteristics of Some Butyrophenones Observed in Cyclohexane Solution and in Solid KBr Matrix

Ketone	$\pi \rightarrow \pi^*$		$\pi \rightarrow \pi^*$	
	λ_{\max}^a Å.	λ_{\max}^b Å.	λ_{\max}^a Å.	λ_{\max}^b Å.
Butyrophenone	3220	3100 ^c	2770	2790
<i>p</i> -Amino			2950	3080
<i>p</i> -Methoxy	3200 ^c	3160	2510	2640
<i>p</i> -Hydroxy			2710	2780
<i>p</i> -Chloro	3250			2500
<i>p</i> -Bromo	3230			2550

^a In cyclohexane solution. ^b In KBr matrix. ^c Weak shoulder.

of the ketones are shifted to the red and the n, π^* bands to the blue. These observations are in agreement with those of Leermakers,²⁶ who studied the electronic spectra of ketones in cyclohexane-silica gel matrix.

The quantum yields of the type-II process of some butyrophenones in KBr matrix are given in Table V. The results show that change of environment to a KBr matrix reduces the quantum efficiency of the unimolecular decomposition of an excited triplet butyrophenone. A possible explanation is the presence of external heavy atoms in the KBr matrix which influences the decay processes from the excited triplet state.²⁷ Furthermore, experiments also show that the

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Table V. Quantum Yields of Butyrophenone Disappearance at 3130 Å. in a KBr Matrix at Various Pressures

Ketone	Pressure, atm.	ϕ
Butyrophenone	10,800	0.005
	6,800	0.01
<i>p</i> -Amino	10,800	0.000
	6,800	0.000
<i>p</i> -Methoxy	10,800	0.000
	6,800	0.000
<i>p</i> -Hydroxy	10,800	0.000
	6,800	0.000
<i>p</i> -Chloro	10,800	0.001
	6,800	0.003

quantum yields decrease with pressure. This effect is perhaps not surprising, since most of the unimolecular decomposition requires that in the transition state, the bonds are stretched before they break, thus giving a greater transition-state volume and a negative pressure effect.

Acknowledgment. The authors are indebted to Mr. E. A. Schuck for some preliminary experimental work and to Dr. J. M. Vernon for helpful discussions. This research was supported by Grant AP109 of the Division of Air Pollution, Bureau of State Services, Public Health Service. E. J. B. also wishes to acknowledge a Public Health Service Special Fellowship 5F3AP-16,569-03 from the Division of Air Pollution.

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Ground States of Conjugated Molecules. IV. Estimation of Chemical Reactivity¹

Michael J. S. Dewar and C. C. Thompson, Jr.

Contribution from the Department of Chemistry, The University of Texas, Austin, Texas 78712. Received November 23, 1964

The semiempirical SCF-MO method described in previous papers of this series²⁻⁴ has been used to calculate localization energies for a number of positions in various aromatic hydrocarbons and the changes in resonance energy when analogous arylmethanes are converted to the corresponding carbanions or carbonium ions. The results are correlated with partial rate factors for substitution in the hydrocarbons, with the relative rates of deprotonation of the arylmethanes with base, and with relative rates of solvolysis for the arylmethyl chlorides.

Introduction

Most of the theoretical work that has been done so far on attempts to predict chemical reactivity has made

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(3) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685 (1965).

(4) M. J. S. Dewar and G. J. Gleicher, *ibid.*, **87**, 692 (1965).

use of the simple Hückel MO method,⁵ or simple variants of it based on the use of perturbation theory.^{5,6} This kind of approach has been quite successful in the case of hydrocarbons; however, it seems to become progressively less reliable for molecules containing increasing numbers of heteroatoms or heteroatomic substituents—a result which is not surprising in view of the known deficiencies of the Hückel method.⁷

Obviously it would be much better if some more refined and reliable approach could be used in such calculations, and the obvious first choice in this connection is the semiempirical SCF-MO method introduced by Pople.⁸ However, attempts to use the Pople treatment in calculations of reactivity have been disappointing, and relatively little work has been done in this field.

(5) See A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

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(7) See, e.g., M. J. S. Dewar, *Rev. Mod. Phys.*, **35**, 586 (1963).

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