

[CONTRIBUTION NO. 3085 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF.]

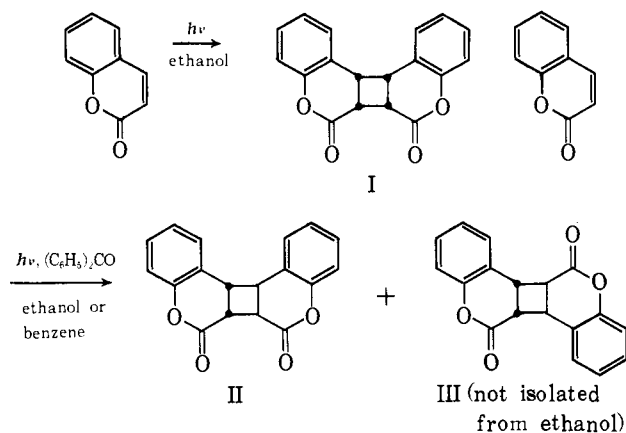
Mechanisms of Photochemical Reactions in Solution. XXV. The Photodimerization of Coumarin¹

BY GEORGE S. HAMMOND, CHARLES A. STOUT,² AND ANGELO A. LAMOLA³

RECEIVED MARCH 3, 1964

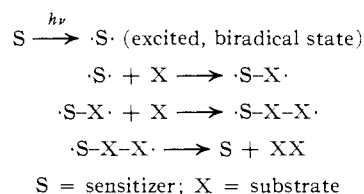
Some details of the mechanism of the direct and sensitized photodimerization of coumarin have been worked out. In nonpolar solvents such as benzene, interaction of excited singlet coumarin with ground state coumarin leads only to self-quenching. In polar solvents such as ethyl alcohol, interaction of excited singlet coumarin with ground state coumarin leads to self-quenching and to the formation of the *cis*-head-to-head dimer (I) in very low yield. In the presence of triplet sensitizers such as benzophenone, the *trans*-head-to-head dimer (II) is formed exclusively in both polar and nonpolar solvents. The formation of the *trans*-head-to-head dimer, which proceeds with a relatively high quantum yield, arises from interaction of excited triplet coumarin and ground state coumarin. In the sensitized reactions, triplet coumarin is produced by energy transfer from the excited triplet sensitizer. In the direct reaction at high dilution, intersystem crossing in coumarin can compete with self-quenching and the *trans*-head-to-head dimer is produced without involving a sensitizer. Benzophenone controls the reaction in ethyl alcohol (*trans*-head-to-head dimer is formed) even when most of the light is absorbed by coumarin. In this case, singlet excitation is transferred from coumarin to benzophenone where intersystem crossing takes place. The triplet excitation is then transferred back to coumarin.

Anet⁴ has reported that irradiation of coumarin in ethanol solution produces a dimer, I, having the *cis* head-to-head structure. In contrast, Schenck, von Wilucki, and Krauch⁵ found that irradiation of benzene solutions containing coumarin and benzophenone led to formation of the *trans* isomer II, along with a trace of the *trans*-head-to-tail dimer III. Irradiation of ethanol solutions containing both coumarin and benzophenone also produced II. Irradiation of benzene solutions containing coumarin but no benzophenone produced no product at all.



Schenck has pointed out that the difference in the results obtained in the presence and in the absence of benzophenone indicate unequivocally that different intermediates must be precursors of I and II. He also concluded that the results were also inconsistent with the view that coumarin is activated by energy transfer from an excited state of benzophenone. The results would be easily understandable if the reactions in the presence of benzophenone are formulated according to the general mechanism suggested by Schenck to account for reactions effected by photosensitizers.

Since we have maintained the view that energy transfer is a key step in many photosensitized reactions, we



were much interested in the reports. Clearly the results do not unequivocally rule out the possible involvement of energy transfer in the benzophenone-controlled reactions. For example, one could maintain that I is formed by attack of an excited singlet state of coumarin on ground state coumarin and that II and III are formed by addition of coumarin triplets to coumarin. In addition, it seemed possible that in one system or the other the isolated product might be formed by photoisomerization of a primary product. Various experiments were carried out to test these hypotheses and have led us to the conclusion that the benzophenone-controlled reaction involves a remarkably complex mechanism involving two intermolecular energy transfers.

Results and Discussion

The possibility of photoisomerization of a primary product was first investigated. Suspensions of I in benzene were irradiated, both with and without benzophenone, for 37 hr. with the unfiltered light of a medium-pressure mercury arc. Similarly, II was irradiated in ethanol solution. In no case was any change observed.

Examination of the details of the earlier experiments⁵ indicated that the effect of benzophenone was not entirely straightforward since the ketone appeared to exert complete control over the course of the reaction despite the fact that most of the light must have been adsorbed by coumarin. In order to define the primary excitation process, irradiations were carried out so that virtually all of the incident light was absorbed by one or the other of the solutes. In all experiments the only product isolated was II. Because of the very low solubility of I, it is certain that no significant amount of that compound was formed. *This was true even in an experiment in which 99.15% of the incident light was absorbed by coumarin.* Since the absorption spectra of the solutions were additive, absorption by benzo-

(1) Part XXIV is D. O. Cowan, M. M. Couch, K. R. Kopecky, and G. S. Hammond, *J. Org. Chem.*, **29**, 1922 (1964).

(2) National Institutes of Health Postdoctoral Fellow, 1962-1963.

(3) National Science Foundation Predoctoral Fellow, 1961-1964.

(4) F. A. L. Anet, *Can. J. Chem.*, **40**, 1249 (1962).

(5) G. O. Schenck, I. von Wilucki, and C. H. Krauch, *Ber.*, **95**, 1409 (1962).

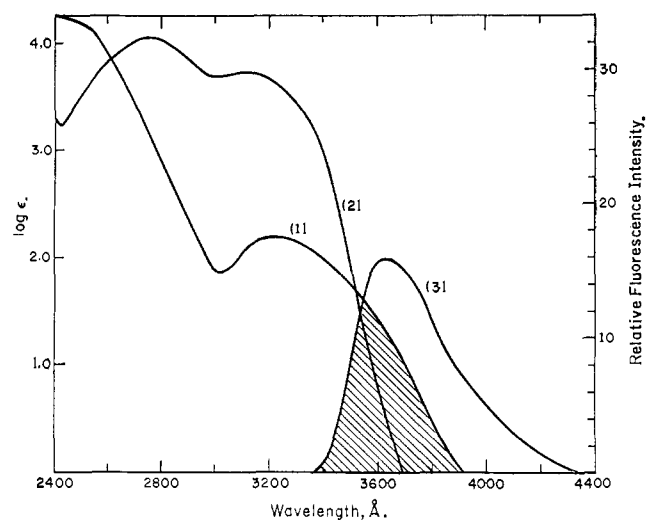
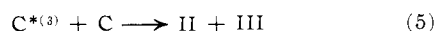
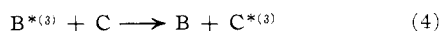
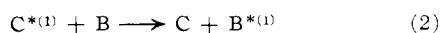


Fig. 1.—Spectra in solution at room temperature of (1) benzophenone absorption (in methyl alcohol), (2) coumarin absorption (in methyl alcohol), and (3) coumarin fluorescence (in ethyl alcohol).

phenone-coumarin complexes cannot have been significant. Apparently benzophenone is not a photosensitizer in the usual sense since it controls the course of the reaction even when it does not absorb the exciting light. The result is consistent with the view that energy acquired by coumarin by absorption is transferred to benzophenone as singlet excitation, and, after intersystem crossing, returned to coumarin as triplet excitation. The *trans* dimers II and III would then be produced by addition of coumarin triplets to the parent compound.



Robust support of the above mechanism was obtained by emission spectroscopy. Solutions of coumarin show structureless fluorescence when irradiated at room temperature. The fluorescence from a dilute absolute ethanol solution has maximum intensity at 3575 Å,⁶ and that from a benzene solution has a maximum at 3640 Å. However, addition of benzophenone quenched the coumarin fluorescence in benzene solution. The quenching reaction is explained by energy transfer by a process such as reaction 2. That transfer might be expected on the basis of the spectra of the two compounds is demonstrated by Fig. 1. There is extensive overlap between the emission spectrum of coumarin and the absorption spectrum of benzophenone.

The emission spectrum of coumarin in ethanol-ethyl ether at 77°K. shows both a short-lived component (fluorescence) and a long-lived component (phosphorescence). The latter has an O-O band at 4590 Å. (62.2 kcal. per mole). Since the excitation energy of benzophenone triplets is 68.9 kcal. per mole, we would expect them to transfer their excitation to coumarin at a diffusion-controlled rate. The relationships among the low-lying excited states of coumarin and benzo-

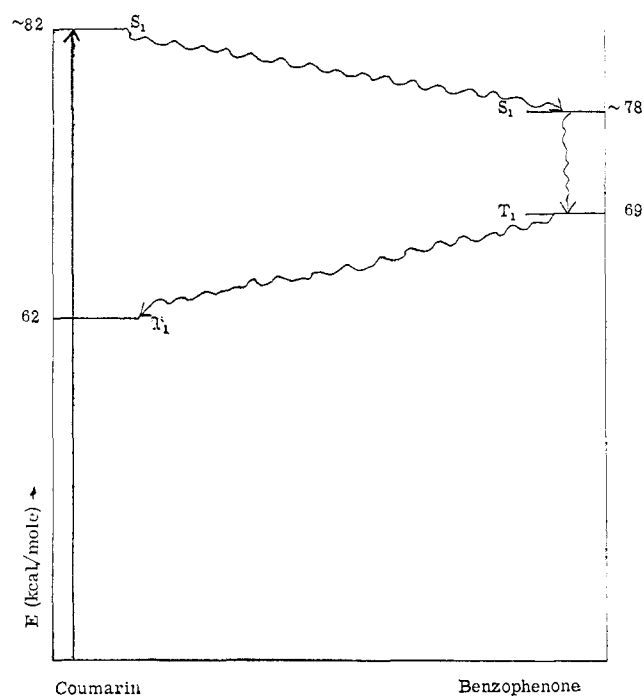


Fig. 2.—The low-lying excited states of coumarin and benzophenone. The fate of excitation absorbed originally by coumarin is traced by the arrows.

phenone which make the double energy transfer possible are shown schematically in Fig. 2. An entirely analogous situation, in which excitation was shuttled between two parts of the same molecule, was reported recently.⁸

Although the spectroscopic evidence seems rather conclusive, some curious features of the photochemistry remain to be accounted for. They are: (1) the fact that I is formed by direct irradiation of coumarin in ethanol, and (2) the fact that no dimer is formed by irradiation of concentrated solutions of coumarin in benzene in the absence of benzophenone. In order to maintain a consistent picture it is necessary to postulate that coumarin singlets are the precursors of I.



The occurrence of reaction 6 is very reasonable at the concentrations used ($\sim 0.3 M$). At such high concentrations there is a finite probability that some pairs of coumarin molecules will be nearest neighbors in solution⁹ and the probability that excited singlets will encounter ground-state molecules during their lifetime ($\tau \cong 10^{-7}$ sec.) is very high. The real problem is to account for the nonoccurrence of reaction 6 in benzene. The dilemma is compounded by the thought that if I is not produced, II probably should be. High conversions of coumarin to II can be effected in the presence of benzophenone in a process to which a triplet mechanism is assigned. Since the fluorescence and phosphorescence spectra of coumarin are of about equal intensity in a glass at 77°K., we must infer that the excited singlets undergo intersystem crossing with significant efficiency. Since II and III are not formed by direct irradiation in solution at room temperature, some process other than reaction 6 must compete with

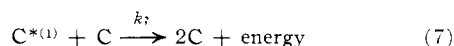
(6) The maximum of fluorescence intensity for a dilute solution of coumarin in 95% ethanol was reported as 3515 Å.⁷

(7) C. E. Wheelock, *J. Am. Chem. Soc.*, **81**, 1348 (1959).

(8) P. A. Leermakers, G. W. Byers, A. A. Lamola, and G. S. Hammond, *ibid.*, **85**, 2670 (1963).

(9) G. S. Hammond and H. P. Waits, *ibid.*, **86**, 1911 (1964).

intersystem crossing. We believe this competitive process must be self-quenching, reaction 7



Since the yield of I is low in ethanol, it is necessary to assume that reaction 7 is the principal mode of destruction of $C^{*(1)}$ in both ethanol and benzene. In ethanol the rate k_6/k_7 is small but measurable; in benzene the ratio is too small to be detectable. This merely indicates that the relative rates of the bimolecular reactions of $C^{*(1)}$ are subject to solvent effects. Since the excited singlet is a polar molecule, one might expect such solvent effects. Intuitively, we expect that the principal effect will show up in reaction 6, the chemical process, but there is no way of making such an allocation on a rigorous basis at this time. That the rate of dimerization relative to self quenching is faster in polar than in nonpolar solvents was demonstrated by direct irradiation in other solvents. In dimethyl sulfoxide, dimethylformamide, and glacial acetic acid compound I was produced. In fact, the conversion rate in acetic acid is considerably faster than in ethanol. Irradiation in dioxane, a less polar solvent, gave no dimer. However, in mixtures of benzene and ethanol or dioxane and ethanol, compound I was formed but at a lower rate than in pure ethanol. Clearly benzene and dioxane do not exert special inhibitory influences.

If the reasoning concerning the fate of $C^{*(1)}$ is correct, intersystem crossing of excited coumarin singlets should be observed in dilute solutions.



Irradiation of a 0.01 *M* solution of coumarin in benzene resulted in production of II. The rate of formation was lower than in experiments with benzophenone, indicating that nonradiative decay of coumarin triplets competes with addition, reaction 5. *The experiment demonstrates that benzophenone is not a necessary agent in the formation of II and proves rigorously that the Schenck mechanism is not an exclusive path for formation of II.* The result also carries the strong implication that energy transfer, rather than addition and elimination, is responsible for the reaction in the presence of benzophenone.

Experimental

Materials.—Coumarin drawn from stock did not bear a supplier's label but was found to have a sharp melting point in agreement with values recorded in the literature. Benzophenone from Matheson Coleman and Bell was used without additional purification. Absolute ethanol and benzene (Baker and Adamson, ACS Reagent Grade) were used without further purification. Dioxane was distilled from the sodium ketyl of benzophenone and stored in the frozen state under nitrogen. Glacial acetic acid (du Pont Reagent Grade) was used as supplied. Dimethyl sulfoxide was stored over a molecular sieve. Dimethylformamide was purified by passage through a column of activated alumina. Fluorenone was Eastman Kodak Reagent Grade. Acetophenone was Matheson Coleman and Bell Reagent Grade. Ethyl coumarate was prepared by the method of Fries and Klostermann.¹⁰ After six recrystallizations from benzene-petroleum ether (with one treatment with activated charcoal) the product was pale yellow, m.p. 87.5–88.5°. The yield of purified product was 5.2 g. (39.5%).

Spectra.—Ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrometer. Emission spectra were measured with a photoelectric spectrophosphorimeter consisting

of a Jarrell Ash Ebert scanning monochromator (*f*/9), and EMI 9558 photomultiplier tube and appropriate recording electronics. Phosphorescence is separated from fluorescence by means of a "rotating can" phosphoroscope which is removed when total emission is measured. Excitation is supplied by a General Electric AH4 mercury lamp with filters suitable for isolation of the group or lines at 3130 and 3660 Å.

The fluorescence from a degassed solution of coumarin in absolute ethyl alcohol (10 mg. in 3 cc.) at room temperature begins at 3400 Å. with maximum intensity at 3575 Å. In benzene at the same concentration and temperature, the coumarin fluorescence begins at 3500 Å. with maximum intensity at 3640 Å. Addition of 20 mg. of benzophenone to the benzene solution completely quenched the coumarin fluorescence.

The phosphorescence and fluorescence emission recorded at 77°K. were for a 0.1 *M* solution of coumarin in a mixture of one part diethyl ether and two parts ethyl alcohol by volume.

Irradiation Procedures.—Irradiations were carried out using an emersion apparatus supplied by the Hanovia Lamp Division of Englehard Industries. The lamp usually used was a 450-watt, medium-pressure, mercury arc, Type Number 679A. A 200-watt lamp was used in some preliminary experiments. Tubes were suspended on the outside of the cylindrical reaction well and the entire assembly was immersed in a large beaker of water. No attempt was made to maintain constant temperature, but the water temperature did not rise above about 35°. Cylindrical glass filters, when used, were placed inside the lamp well. Filter solutions were placed in the well jacket providing a 1.8-cm. liquid-filter layer. Unless otherwise specified, the ampoules were prepared from Pyrex test tubes having a 25-mm. diameter. After loading, the tubes were flushed with a stream of nitrogen and sealed.

Absence of Complexes.—Solutions containing 0.1 *M* benzophenone and coumarin were mixed and their absorbances were measured in the spectral region between 3850 and 4100 Å. No departure from additivity was observed in either methanol or benzene.

Direct Irradiation in Ethanol.—A solution of 12.3 g. of coumarin was divided among three tubes. The tubes were degassed, sealed *in vacuo*, and irradiated without a filter with the 200-watt lamp for 72 hr. The tubes were opened and the crystalline product was removed by filtration and recrystallized from glacial acetic acid. The yield of I, m.p. 272–274°, was 1 g. (8%). The results essentially duplicate those of Anet.⁴

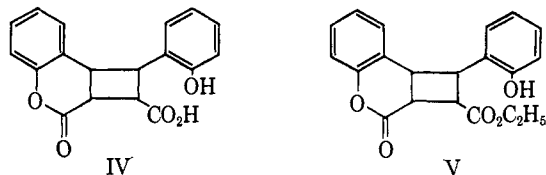
Effects of Benzophenone.—A solution containing 3.65 g. (0.5 *M*) coumarin and 14.3 g. (1.57 *M*) benzophenone in 50 ml. of benzene was divided between two Pyrex tubes and irradiated for 75.5 hr. filtering the light with uranium glass which is opaque to light of wave lengths shorter than 3340 Å. Virtually all the absorbed light was in the 3660 Å. mercury line. Since the ratio ϵ_B/ϵ_C is 94 at 3650, 98% of the exciting light was adsorbed by the benzophenone. The contents of the two tubes were combined and the solvent was removed by evaporation. The residual oil slowly became a crystalline crust after cooling. The crystals were washed with benzene and vacuum dried. The residue was 1.234 g. (33.8%) of crude II, m.p. 163–165°.

A solution containing 7.3 g. of coumarin (0.5 *M*) and 0.91 g. (0.05 *M*) of benzophenone was divided among three Pyrex tubes and irradiated through a filter solution prepared by dissolution of 46 g. of $\text{NiSO}_4 \cdot \text{H}_2\text{O}$ and 14 g. of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ in 100 ml. of water. One-cm. layers of the solution have optical densities of 2.15, 0.23, 0.025, and 0.001 at 3660, 3341, 3130, and 3025 Å., respectively. Using these data, the spectral distribution for Hanovia Lamp No. 679A as described by the supplier, and the extinction coefficients of coumarin and benzophenone at the four wave lengths, we estimate that 99.15% of the exciting light was absorbed by coumarin. The irradiation was carried out for 80 hr. and the product was isolated in the usual manner by recrystallization from benzene. The yield of II was 0.571 g. (7.8%).

In three parallel experiments 3.48-g. samples of coumarin were dissolved in 25 ml. of dioxane along with sufficient benzophenone to make the solutions 0.11, 0.011, and 0.0013 *M* with respect to the latter solute. The tubes were irradiated with the unfiltered light from the 450-watt lamp. The first two tubes were irradiated 82 hr., the third for 79.5 hr. The products were isolated as usual and recrystallized several times from benzene; the yields from tubes 1 and 2 were 2.77 (79.5%) and 2.68 g. (76.7%) of II. The product from the third tube was recrystallized from ethyl acetate-toluene mixture giving a new material, m.p. 159.6–161.9°. On melting, the material evolved a gas, resolidified,

(10) K. Fries and W. Klostermann, *Ann.*, **362**, 1 (1908).

and remelted at 178.8–179.3°, the melting point of II. The infrared spectrum of the material had bands, *inter alia*, at 3410, 1755, and 1710 cm⁻¹. The product is believed to be a mixture of IV and V, and is probably formed by reaction with water and ethanol during isolation.



The combined weight of all fractions was 0.506 g. (~15%). Since a different material was isolated, the yield cannot be compared with those in the parallel experiments, but the result does show that dimerization occurs even with a coumarin:benzophenone ratio of 720.

Effect of Acetophenone.—A solution of 3.48 g. of coumarin and 0.06 g. of acetophenone in 25 ml. of benzene was irradiated in a Pyrex tube for 79.5 hr. The product was recrystallized from ethyl acetate–toluene giving 392 mg. (11%) of a material that melted at 159.6–161.9° with evolution of a vapor, resolidified, and remelted at 178.8–179.3°, the melting point of II. The product initially isolated is believed to be VI and/or V formed by ring opening by adventitious water or alcohol during isolation (*vide supra*).

Effect of Fluorenone.—A solution of 3.48 g. of coumarin and 0.06 g. of fluorenone in 25 ml. of benzene was irradiated in a Pyrex tube for 79.5 hr. with unfiltered light. Two products were isolated, 441 mg. (12.7%) of II and 856 mg. (24%) of the ring-opened product (*vide supra*) derived from II.

Direct Irradiation in Benzene at High Dilution.—Twenty 12 × 100 mm. Kinnex tubes were loaded with 3 ml. each of 0.01 M solutions of coumarin in benzene. The solutions were degassed with three freeze–thaw cycles, sealed *in vacuo*, and irradiated for 71 hr. with unfiltered light from the 450-watt lamp. The contents of the tubes were combined and solvent was removed by evaporation under a stream of air. The residual scum was taken up in hot toluene and after four recrystallizations yielded 10 mg. (11%) of II, m.p. 179.8–180.6°. The infrared spectrum was identical with that of pure II.

Direct Irradiation in Benzene–Ethanol.—A 16-g. sample of coumarin was dissolved in a mixture of 100 ml. of benzene and 25 ml. of ethanol and divided among four Pyrex tubes. The solutions were flushed with nitrogen, sealed, and irradiated with unfiltered light for 94 hr. The product was isolated and recrystallized from glacial acetic acid, giving 320 mg. (2%) of I.

Direct Irradiation in Dioxane–Ethanol.—A solution of 3 g. of coumarin in 2 ml. of ethanol and 2 ml. of dioxane was placed in a Pyrex tube, flushed with nitrogen, sealed, and irradiated for 82 hr. with unfiltered light. The yellow solution was worked up as usual, yielding 24 mg. (0.8%) of I after one recrystallization.

Irradiation in Dimethyl Sulfoxide.—A solution of 3.48 g. of coumarin in 30 ml. of DMSO was irradiated in five nitrogen-flushed, Pyrex tubes with unfiltered light for 76.5 hr. The yellow solution was concentrated at 1 mm., leaving a viscous yellow residue. Benzene was added and crystals slowly formed. The infrared spectrum of the product was identical with that of an authentic sample of I; yield 130.8 mg. (3.7%).

Irradiation in Dimethylformamide.—The experiment was a duplicate of the previous one except that the solvent was 30 ml. of DMF. The yield of I was 70.3 mg. (2%).

Irradiation in Acetic Acid.—The experiment was a duplicate of the previous two except that 3.0 g. of coumarin was dissolved in 30 ml. of glacial acetic acid and irradiation was terminated after 48 hr. The yield of I was 0.643 g. (21.4%).

Irradiation of Ethyl Coumarate.—A solution of 1.01 g. of ethyl coumarate in 30 ml. of benzene was degassed, sealed *in vacuo*, and irradiated in a Pyrex tube with unfiltered light for 72.5 hr. Only coumarin was isolated from the mixture.

An identical experiment was carried out with 0.99 g. of benzophenone added to the mixture. A crystalline product which separated during irradiation was recrystallized three times from benzene and sublimed *in vacuo* to give 50 mg., white crystals, m.p. 198°. The product was not further investigated.

A solution containing 1.005 g. of ethyl coumarate and 0.102 g. of coumarin in 30 ml. of benzene was degassed and irradiated with unfiltered light for 72.5 hr. Only coumarin could be isolated from the mixture.¹¹

Acknowledgment.—This study was partially supported by a grant from the National Science Foundation.

(11) NOTE ADDED IN PROOF.—Recent measurements suggest strongly that transfer of singlet energy from coumarin to benzophenone involves emission and reabsorption of light.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY, PITTSBURGH 13, PENNA.]

Chemical Behavior of Charge-Transfer Complexes. II. Phenanthrene Catalysis in Acetolysis of 2,4,7-Trinitro-9-fluorenyl *p*-Toluenesulfonate^{1,2}

BY ALLAN K. COLTER, SAMUEL S. WANG, GEORGE H. MEGERLE, AND PAUL S. OSSIP

RECEIVED MARCH 16, 1964

Acetolysis of 2,4,7-trinitro-9-fluorenyl *p*-toluenesulfonate (I) is accelerated by added phenanthrene. Rates of acetolysis were measured at a series of phenanthrene concentrations at 55.85, 70.0, 85.0, and 99.9°. Rates increase with increasing phenanthrene concentration up to 5.16 times the uncatalyzed rate at 0.086 M phenanthrene (70.0°), the highest concentration studied. Apparent (formal) activation parameters (70.0°) vary from $\Delta H^\ddagger = 25.7$ kcal. mole⁻¹, $\Delta S^\ddagger = -11.7$ e.u. mole⁻¹, in the absence of phenanthrene, to $\Delta H^\ddagger = 22.4$ kcal. mole⁻¹, $\Delta S^\ddagger = -18.3$ e.u. mole⁻¹ at 0.08 M phenanthrene. The data were analyzed in terms of a mechanism involving 1:1 complexing between phenanthrene and substrate. The analysis leads to values of K_T , the equilibrium constant for 1:1 complex formation, and k_c , the specific rate of acetolysis of the 1:1 complex, at 55.85, 70.0, and 85.0°. The 1:1 complex is 21 to 27 times as reactive in acetolysis as uncomplexed substrate at these temperatures. Values of K_T are in good agreement with values estimated by an independent spectrophotometric study. Activation parameters for acetolysis of the 1:1 complex were estimated to be $\Delta H^\ddagger \approx 26$ kcal. mole⁻¹ and $\Delta S^\ddagger \approx -5$ e.u. mole⁻¹, showing that the 1:1 complex is more reactive in acetolysis than the uncomplexed substrate because of a more favorable entropy of activation. The significance of these results is discussed.

Introduction

The field of organic molecular complexes of the donor–acceptor type has been a very active one during the past

decade.³ However, relatively little attention appears to have been given to the possible effects of complex

(1) A preliminary report of a portion of this work has appeared: A. K. Colter and S. S. Wang, *J. Am. Chem. Soc.*, **85**, 115 (1963) (part I of this series).

(2) Abstracted in part from a thesis submitted by S. S. Wang in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology, June, 1961.

(3) G. Briegleb, "Electronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961.