Dynamics of the Wolff Rearrangement of Six-Membered Ring o-Diazo Ketones by Laser Flash Photolysis[†]

Katsumi Tanigaki^{*,‡} and Thomas W. Ebbesen^{*,‡,§}

Fundamental Research Laboratories, NEC Corporation, 4-1-1 Miyazaki, Miyamae-ku, Kawasaki 213, Japan, and Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556 (Received: November 7, 1988)

The Wolff rearrangement of six-membered ring o-diazo ketones, 1-oxo-2-diazo-1,2-dihydronaphthalene (DNQ) and its four 4- and 5-sulfonate analogues, 1-oxo-2-diazo-1,2-dihydrobenzene (DBQ), and diazoMeldrum (DM), are studied in solution at room temperature by laser flash photolysis. A presursor to a ketene is observed in most cases. It is assigned to be an oxirene on the basis of reactivity, kinetic results, and thermodynamic results. The Wolff rearrangement does not involve a concerted mechanism but a stepwise reaction for these types of diazo ketones. Thermodynamic analyses indicate that the activation barriers for the transformation of the oxirenes into ketenes are very low, typically 10-20 kJ/mol, in good agreement with theoretical predictions in the literature. The observation of oxirene in solution in nanosecond time scales, and longer, is attributed to the low preexponential factors due to the negative entropy of solvation. The important role of the solvent is further confirmed in the kinetic analysis of ketene formation in various water-methanol mixtures.

Introduction

Rearrangement reactions of nitrogen, oxygen, or carbon play very important roles in chemistry. Among them, the Wolff rearrangement, which involves a carbon atom 1,2 migration, is of great importance and interest in organic synthesis and photochemistry.¹ The photolysis of o-diazo ketones yields very reactive ketene intermediates through the Wolff rearrangement, and these ketenes may undergo a variety of reactions.² The Wolff rearrangement is known to be incorporated in the Arndt-Einstert synthesis,³ in which an acid is converted to its next higher onecarbon homologue. Ring contraction of cyclic o-diazo ketones is a general method for the preparation of strained small-ring compounds.⁴ Racemization, which is important in optically active synthesis, has also been discussed with regard to the Wolff rearrangement.⁵ The change in the chemical properties of o-diazo ketones by photolysis is currently used in the photolithographic industry.6

Although the chemistry of the Wolff rearrangement has been widely used in many fields, the mechanism of the Wolff rearrangement is still being debated.⁷ The focus of the discussion on the Wolff rearrangement is whether it is a concerted reaction, where dinitrogen loss occurs at the same time as the 1,2 migration of a carbon atom, or a stepwise reaction where some precursors exist before the ketene formation, as shown in Figure 1. Furthermore, if a precursor does exist, what is its nature: a ketocarbene and/or an oxirene-like intermediate? In this article we try, among other things, to answer these two questions. However, one must keep in mind that such aspects will depend on the type of o-diazo ketones used in the study.

For instance, the product ratio observed in direct and triplet sensitized photolysis of nonaromatic o-diazo ketones required Tomioka et al. to postulate a concerted rearrangement occurring from the s-Z conformation and a nonconcerted rearrangement occurring from the s-E conformation of their compounds.⁸

In another study, Chapman et al. sought a system in which the Wolff rearrangement would be suppressed and could be followed with low-temperature matrix isolation.⁹ They demonstrated that increasing strain in the transition state for ring contraction suppressed the Wolff rearrangement, and thereby, they succeeded in trapping ketocarbene with these compounds. However, these five-membered ring o-diazo ketones do not undergo the Wolff rearrangement thermally or photochemically in solution or thermally in the gas phase, while strain-free six-membered ring o-diazo ketones usually do. These facts indicate that the strain of the transition state is very important. Hence, the features of the Wolff rearrangement of strained o-diazo ketones are considered to be different from those of "strain-free" o-diazo ketones such as studied here.

From the thermal and photochemical experiments with unsymmetrically substituted diazo ketones¹⁰ and from label scrambling in isotopically labeled diazo ketones,¹¹ ketocarbene-keto-carbene interconversion has been explained by the existence of an oxirene or an oxirene-like compound.^{10,11} Several theoretical calculations¹² predict oxirene to be an energy minimum with a low barrier for rearrangement to a ketene. All these species are expected to be short-lived transients. However, until very recently, there have been relatively few studies using time-resolved techniques, such as laser flash photolysis, to try to detect the reaction intermediates of the Wolff rearrangement.^{13,14} Two earlier

M., Jr.; Moss, R. A. Carbenes; R. E. Krieger: Malabar, FL, 1983; Vol. I, pp 117-125. (d) Moss, R. A.; Jones, M., Jr. Carbenes; R. E. Krieger: Malabar, FL, 1983, Vol. II, pp 88-90.
(2) (a) Lewars, E. G. Chem. Rev. 1983, 83, 519. (b) Torres, M.; Lown, E. M.; Gunning, H. E.; Strausz, O. P. Pure Appl. Chem. 1980, 52, 1623. (c) Hendrickson, J. B.; Cram, D. J.; Hammond, G. S. Organic Chemistry, 3rd ed.; McGraw-Hill Kogakusya: Tokyo, 1970, pp 701-703. (d) Chemistry of Alkenes; Patai, S., Ed.; Interscience: New York, 1964; p 1161.
(3) Arndt, F.; Eistert, B. Chem. Ber. 1935, 68, 200.
(4) Redmore, D.; Gutsche, C. D. Adv. Alicyclic Chem. 1971, 3, 125.
(5) Lane, J. F.; Weissberger, A.; Wallis, E. S. J. Org. Chem. 1940, 5, 276.
(6) (a) Thompson, L. F.; Willson, C. G.; Bowden, M. J. S. Introduction to Microlithography; American Chemical Society: Washington, DC, 1984.
(b) Deforest, W. S. Photoresist Materials and Processes; McGraw-Hill: New York, 1975. (c) Dinaburg, M. S. Photosensitive Diazo Compounds; Focal

- York, 1975. (c) Dinaburg, M. S. Photosensitive Diazo Compounds; Focal Press: New York, 1964.

Press: New York, 1964.
(7) For an example, see: ref 1a, p 476.
(8) (a) Tomioka, H.; Okuno, H.; Izawa, Y. J. Org. Chem. 1980, 45, 5278.
(b) Tomioka, H.; Kondo, M.; Izawa, Y. J. Org. Chem. 1981, 46, 1090.
(9) (a) Hayes, R. A.; Hess, T. C.; McMahon, R. J.; Chapman, O. L. J. Am. Chem. Soc. 1983, 105, 7786. (b) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H.-P. J. Am. Chem. Soc. 1985, 107, 1507 7597

(10) (a) Cormier, R. A. Tetrahedron Lett. 1980, 2021. (b) Matlin, S. A.; Sammer, P. G. J. Chem. Soc., Perkin Trans. 1 1972, 2623

(11) (a) Blaustein, M. A.; Berson, J. A. Tetrahedron Lett. 1981, 22, 1081. (b) Zeller, K.-P. J. Chem. Soc., Chem. Commun. 1975, 317. (c) Zeller, K.-P. Angew. Chem., Int. Ed. Engl. 1970, 16, 781. (d) Timm, U.; Zeller, K.-P.; Meier, H. Tetrahedron 1977, 33, 463. (12) (a) Tanaka, K.; Yoshimine, M. J. Am. Chem. Soc. 1980, 102, 7655.

(b) Csizmadia, I. G.; Gunning, H. E.; Gosavi, R. K.; Strausz, O. P. J. Am. Chem. Soc. 1973, 95, 133. (c) Dewar, M. J. S.; Ramsden, C. A. J. Chem. Soc., Chem. Commun. 1973, 688. (d) Bouma, W. J.; Nobes, R. H.; Radom, L.; Woodward, C. E. J. Org. Chem. 1982, 47, 1869.

Document No. NDRL-3088 from the Notre Dame Radiation Laboratory. [‡]NEC Corporation.

[§] University of Notre Dame.

⁽¹⁾ For reviews, see: (a) Kirmse, W. Carbene Chemistry, 2nd ed.; Academic Press: New York, 1971; Vol. I, pp 475-496. (b) Ershov, V. V.; Nikiforov, G. A.; De Jonge, C. R. H. I. *Quinone Diazides*; Studies in Organic Chemistry 7; Elsevier Scientific: New York, 1981; pp 261-270. (c) Jones, M. J.r.; Moss, R. A. *Carbenes*; R. E. Krieger: Malabar, FL, 1983; Vol. I, pp 117-125. (d) Marge B. A. Large M. E. Criberto D. E. Krieger: Malabar, FL, 1983; Vol. I, pp



Figure 1. Reaction scheme after excitation of o-diazonaphthoquinone: KC, ketocarbene; OX, oxirene; and KE, ketene. The carbon atom migration of KC/OX to KE is called the Wolff rearrangement.



Figure 2. Structures and abbreviations of six-membered ring o-diazo ketones used in this study.

microsecond flash photolysis studies¹⁵ of o-diazo ketones failed to detect any species other than ketenes.

Using nanosecond laser flash photolysis, the Wolff rearrangement for various six-membered ring o-diazo ketones is examined, and it is found that the results given in a preliminary communication¹⁴ for sodium 1-oxo-2-diazo-1,2-dihydronaphthalene-5-sulfonate are quite general. The mechanism is always a stepwise reaction. The assignment of the precursor of ketene to oxirene is further confirmed by analyzing the thermodynamics and solvent dependence of the reactions.

Experimental Section

As representative six-membered ring o-diazo ketones, the following compounds, shown in Figure 2, were studied: 1-oxo-2-diazo-1,2-dihydronaphthalene-4- and -5-sulfonate sodium salts (DNQ-4S, DNQ-5S), 1-oxo-2-diazo-1,2-dihydrobenzene (DBQ),



Figure 3. Infrared spectra of DNQ-5STL isolated in an argon matrix at 22.3 K (a) before exposure and (b) after exposure to light.

TABLE I:	Infrared Spec	trum Change:	s for DNQ-4	STL, DNQ-5STL,
DNQ, and	DM Isolated	in Argon Mat	rix at 22.3	K before and after
Exposure (cm ⁻¹)	-		

compd	-N ⁺ =N ^{-a}	C=O ^a	$C = C = O^b$	
DNQ	2102.0	1642.0	2120.0	
DNQ-4STL	2131.5	1641.6	2135.4	
DNQ-5STL	2212.6	1641.6	2216.8	
DM	2174.0	1744.0	2140.0	
	2162.0			

^aBefore exposure. ^bAfter exposure.

1-oxo-2-diazo-1,2-dihydronaphthalene (DNQ), 4-tolyl 1-oxo-2diazo-1,2-dihydronaphthalene-4- and -5-sulfonates (DNQ-4STL, DNQ-5STL), and 2,2-dimethyl-4,6-dioxo-5-diazo-1,3-dioxolane (diazoMeldrum; DM). The compounds were prepared by standard procedures described in the literature.¹⁶

Low-Temperature Matrix-Isolated Infrared Spectra. The system used in this study was similar to the one reported by Chapman et al.¹⁵ Samples were allowed to sublime and were isolated in an argon matrix at 22.3 K. The samples isolated in argon were exposed to light through a Toshiba UV-31 filter and then infrared spectra were measured.

Nanosecond Laser Flash Photolysis. The nanosecond laser flash photolysis was carried out with a Molectron UV 400 N₂ laser (337 nm, <4 mJ) or, in the case of DM, with a Lamba Physik EMG 101 MSC (248 nm). The analysis path length was either 2 or 10 mm depending on the experiments, and a flow cell was employed due to the rapid photodegradation of the samples. Each experimental point is the average of several transient signals recorded by a computer-controlled system.

Results

1. Low-Temperature Matrix Isolation of Intermediates. Before any kinetic studies could be undertaken, it was necessary to confirm that the compounds studied here form the well-known ketene intermediates during photolysis, i.e., that the Wolff rearrangement really occurs. For this purpose we used the lowtemperature matrix isolation technique in argon at 22.3 K and

⁽¹³⁾ Delaire, J. A.; Faure, J.; Hassine-Renou, F.; Soreau, M. New J. Chem. 1987, 11, 15.

⁽¹⁴⁾ Tanigaki, K.; Ebbesen, T. W. J. Am. Chem. Soc. 1987, 109, 5883.
(15) (a) Nakamura, K.; Udagawa, S.; Honda, K. Chem. Lett. 1972, 763.
(b) Bolsing, F.; Spanuth, E. Z. Naturforsch. B: Anorg. Chem., Org. Chem., 1976, 31B, 1391.

^{(16) (}a) Anderson, J. P. C.; Le Feure, R. J. W.; Wilson, I. R. J. Chem. Soc. 1949, 2082.
(b) Yates, P.; Robb, E. W. J. Am. Chem. Soc. 1957, 79, 5760.
(c) Ershov, V. V.; Nikiforov, G. A.; DeJonge, C. R. H. I. Quinone Diazides; Studies in Organic Chemistry 7; Elsevier Scientific: New York, 1981.
(d) Regitz, M.; Hocker, J.; Liedhegener, A. In Organic Synthesis; Wiley: 1973; Coll. Vol. 5, p 179.



Figure 4. (a) Absorption spectra of DNQ-5S (solid curve) and the final photolytic product in water (dashed curve). (b) Transient spectra observed upon laser excitation of DNQ-5S in water at 337 nm: the first transient A (\bullet -marked solid curve) and the second transient B (Δ -marked dashed curve). (c) Transient spectra in methanol: the transient B (Δ -marked dashed curve) and final product C (×-marked dotted curve).

the formation of ketenes was checked by infrared (IR) spectroscopy.

Figure 3 shows an example of the IR spectra for DNQ-5STL measured at 22.3 K in an argon matrix. Irradiation (>310 nm, 5 min) of the DNQ-5STL isolated in an argon matrix 22.3 K gave the corresponding indenoketene. The structural assignment is based on the appearance of the intense infrared ketene stretching vibration ($v_{C=C=O}$) at 2216.8 cm⁻¹, and the disappearance of the diazo stretching vibration $(\upsilon_{-N=-N})$ and the cyclic ketone stretching vibration ($v_{C=0}$) at 2212.6 and 1641.6 cm⁻¹, respectively. Equivalent changes were also observed for the other compounds. The changes in the IR spectra for DNQ-5STL, DNQ-4STL, DNQ, and DM before and after exposure are listed in Table I. These results confirm that all the compounds studied here undergo the photochemical reaction involving the Wolff rearrangement. It is noted that the ketene stretching vibration $(v_{C=C=O})$ appeared at a lower wavenumber than the diazo stretching vibration $(v_{-N=N})$, for DM. This is in contrast with the other compounds.

2. Nanosecond Laser Flash Photolysis. a. Transient Spectra in Water and Methanol. Figures 4-8 give the transient spectra observed upon excitation of various diazo ketones in water and methanol with nanosecond laser flash photolysis. For the water-soluble diazo ketones, such as DNQ-5S, DNQ-4S, DBQ, and DM, the transient spectra in water and methanol can be directly compared as in Figures 4, 5, 6, and 7. For DNQ-5S (Figure 4b) and DNQ-4S (Figure 5b) the first transient A that appears within the laser pulse in water absorbs at shorter wavelengths than the second transient B, to which the first transforms



Figure 5. (a) Absorption spectra of DNQ-4S (solid curve) and the final photolytic product in water (dashed curve). (b) Transient spectra observed upon laser excitation of DNQ-4S in water at 337 nm: the first transient A (\bullet -marked solid curve) and the second transient B (Δ -marked dashed curve). (c) Transient spectra in methanol: the transient B (Δ -marked dashed curve) and final product C (×-marked dotted curve).

within $\sim 1 \ \mu s$. The first transient observed in methanol resembles very much the second transient observed in water as shown in Figures 4c and 5c. Kinetic analyses, to be presented below, confirm that these are the same species and that transient A converts to transient B faster than our resolution in pure methanol. Hence the first transients observed in methanol in Figures 4c and 5c correspond to the transients B in water.

In the case of DBQ, the first (A) and second (B) transients are observed both in water and in methanol as shown in Figure 6, although the transformation of A into B is much faster in methanol than in water. In contrast, flash photolysis of DM reveals only one short-lived transient in water as shown in Figure 7b, but two in methanol as shown in Figure 7c, where the rate of the transformation from A to B increases with water content in solution.

Figure 8 shows the transient spectra observed for DNQ, DNQ-5STL, and DNQ-4STL in methanol. Only one short-lived transient spectrum was observed for these *o*-diazo ketones, which resembles the corresponding transient at B for the other DNQ's shown in Figures 4 and 5.

The transient species just reported eventually decay to give a third species C. Those spectra are given by the \times -marked curves in Figures 4–8, when they were observable. When the transformation of B into C was very slow, the transient spectra of C could not be recorded with any accuracy, although the dynamics was observed at a single wavelength. Before assigning transients A, B, and C to any chemical species shown in the reaction scheme in Figure 1, their kinetics and reactivity in various conditions are assessed in the next paragraphs.

b. Kinetics and Solvent Effects. The rate of the transformation of A and B (k_{AB}) and B into C (k_{BC}) were analyzed under various conditions. k_{AB} is independent of wavelengths, concentrations of the parent molecules, and laser intensity (i.e., the concentration of transient A). The transformation of A into B is a first-order reaction. Table II gives the values of k_{AB} for the diazo ketones studied here. It can be noticed that its value is always larger in methanol than in water except for DM, where the reverse is true. To verify that in pure methanol (or pure water in the case of DM)



Figure 6. (a) Absorption spectra of DBQ (solid curve) and the final photolytic product in water (dashed curve). (b) Transient spectra observed upon laser excitation of DBQ in water at 337 nm: the first transient A (\bullet -marked solid curve) and the second transient B (Δ -marked dashed curve). (c) Transient spectra in methanol: the transient A (\bullet -marked solid curve), the transient B (Δ -marked dashed curve), and final product C (\times -marked dotted curve).



Figure 7. (a) Absorption spectra of DM (solid curve) and the final photolytic product in water (dashed curve). (b) Transient spectra observed upon laser excitation at 254.7 nm of DM in water: the transient B (Δ -marked dashed curve). (c) Transient spectra in methanol: the transient A (\bullet -marked solid curve) and the transient B (Δ -marked dashed curve).

 k_{AB} is indeed too fast to be observed within our time resolution, the ratio of the water-methanol mixture was varied. The results



Figure 8. Transient spectra for (a) DNQ-5STL, (b) DNQ-4STL, and (c) DNQ in methanol: the transients B (Δ -marked dashed curves) and the final product C (×-marked dotted curve).



Figure 9. Dependence of water-methanol mixtures on transformation rates of A to B: (a) DBQ (O-marked curve) and DNQ-5S (\bullet -marked curve); (b) DM (×-marked curve).

TABLE II: Rate Constants of Transients A and B in Water and Methanol

		k _{AB} ^a		k _{BC}	
compd	solvent	k4 or k_2	ks ^b	$k_{\mathbf{K}}^{c}/\epsilon_{\mathbf{k}}^{d}$	k _G e
DNQ-4SNa	H ₂ O	1.3×10^{7}	4.9×10^{2}	n.o. ^f	n.o.
	MeOH	>108	3.0×10^{6}	n.o.	n.o.
DNQ-5SNa	H ₂ O	3.0×10^{6}	1.8×10^{3}	n.o.	n. o.
	MeOH	>108	3.2×10^{6}	n.o.	n.o.
DNQ-4STL	MeOH	>108	1.5×10^{3}	1.2×10^{4}	n.o.
DNQ-5STL	MeOH	>108	5.5 × 10⁴	2.8×10^{5}	n.o.
DNQ	MeOH	>108	2.0×10^{5}	1.2×10^{4}	n.o.
DBQ	H_2O	7.6×10^{5}	3.5×10^{2}	n.o.	n.o.
	MeOH	5.8×10^{6}	1.3×10^{6}	n.o.	n.o.
DM	H ₂ O	>108	1.5×10^{3}	n.o.	n.o.
	MeOH	2.8×10^{5}	5.0×10^{3}	n.o.	n.o.

 ${}^{a}k_{AB}$, s⁻¹. ${}^{b}k_{S}$, s⁻¹. ${}^{c}k_{K}$, M⁻¹ s⁻¹. ${}^{d}\epsilon_{k}$, absorption coefficient of ketene. ${}^{c}k_{G}$, M⁻¹ s⁻¹. f Not observed in our conditions.

are shown in Figure 9a for DBQ and DNQ-5S and Figure 9b for DM. With percent volume of methanol, the rate increases linearly

TABLE III: Activation Energies, E, (kJ/mol), and Frequency Factors, Z

compd/solvent	Ea	Z	
DNQ-4SNa/H ₂ O	18.2	3 × 10 ⁹	
DNQ-5SNa/H ₂ O	18.7	6×10^{10}	
DBQ/H ₂ O	22.8	9 × 10 ⁹	
DBQ/MeOH	12.4	1 × 10 ⁹	
DM/MeOH	16.8	2.5×10^{8}	

for DBQ, while the dependence is even stronger for DNQ-5S as shown in Figure 9a. k_{AB} for DM is very sensitive to the water content and shows a linear dependence in the range that could be investigated (Figure 9b). These results confirm that the first transient observed in methanol for DNQ's and the first transient observed in water for DM correspond to the second transients B in water and methanol, respectively.

Other potential effects on k_{AB} were also investigated. Highly acidic conditions, either 0.1 N HCl or acetic acid (pH = 2), do not change k_{AB} for DNQ-5S in water. Similarly, high ionic strength (0.1 M LiClO₄) and O₂ do not affect this rate.

While transient A and its transformation into B are insensitive to acid, transient B (and $k_{\rm BC}$) is largely affected by both solvents and acidic conditions. The disappearance of transient B of DNQ-5S is accelerated by over 2 orders of magnitude at high pH (acetic acid, pH = 2). The rates k_{BC} for the decay of the transients B in pure water and methanol are given in Table II. No dependence on the initial diazo ketone concentration was detected at concentrations less than 7×10^{-4} M (as used here). In most cases, $k_{\rm BC}$ is a first-order rate and is only sensitive to the solvent. In the case of DNQ-5STL and DNQ-4STL, the disappearance of B is also dependent on the concentration of B, when the latter is varied with the laser intensity. Analysis of the kinetic dependence for various laser intensities and various concentrations of parent diazo ketones, using the method of Bensasson and Gramain,¹⁷ gives a first-order rate constant $k_{\rm S}$, a second-order rate constant $k_{\rm K}$ due to the bimolecular reaction **B** + **B**, and a rate constant k_{G} due to the reaction of B + G, where G denotes the parent diazo ketone. In Table II, the bimolecular rate constants are given in the form $k_{\rm K}/\epsilon_{\rm k}$, because the extinction coefficients of B (ϵ_k) are unknown. As mentioned above, no effect of [G] could be detected in our experimental conditions.

c. Temperature Dependence. In order to identify transients A and B more clearly in terms of the reaction scheme in Figure 1, the potential barrier of the transformation of A into B was measured for some of the diazo ketones. This information will be useful since the potential barriers on going from ketocarbene or oxirene to ketene (see Figure 1) have been estimated by thorough theoretical studies.¹² The rates k_{AB} were measured for DNQ-5S, DNQ-4S, DBQ, and DM at various temperatures. Figure 10 shows the corresponding Arrhenius plots according to the Arrhenius equation $k_{AB} = Z \exp(-E_a/RT)$, where Z is the frequency factor, E_a the potential barrier, T the temperature, and R the gas constant. The values for Z and E_a extracted from these plots are given in Table III. The potential barriers are only 10-20 kJ/mol for the four different molecules, and the barrier drops by nearly a factor of 2 for DBQ when the solvent is changed from water to methanol. With such low potential barriers, the reaction rate would be much faster, were it not for the low frequency factor Z. The low values of Z correspond to negative entropies of activation which are most likely due to the rearrangement of the solvent molecules during the transformation of A into B. The strong effect of solvent composition on k_{AB} shown earlier (Figure 9) is in clear agreement with these thermodynamic results, and together, they indicate the important role of solute-solvent interactions in this reaction.

Discussion

The Wolff rearrangement and the possible reactions of ketene are schematically summarized in Figure 1. Looking at the reaction



Figure 10. Arrhenius plots of transformation of transient A into B: D, $DNQ-4S/H_2O; \times, DBQ/MeOH; \bullet, DNQ-5S/H_2O; \Delta, DBQ/H_2O; *,$ DM/MeOH.

scheme, there are at least two or three possible intermediates, ketocarbene (KC), oxirene (OX), and ketene (KE), involved in the formation of the final products of the Wolff rearrangement. It would be difficult to identify transients A and B in terms of these intermediates, solely on the basis of their absorption spectra. However, combined with the kinetic measurements, the solvent dependence and the thermodynamic data, a reasonable interpretation of the results can be undertaken in conjunction with reports in literature.

Transient B can be most confidently assigned to be a ketene. The differential absorption spectra of the DNQ's as shown in Figures 4, 5 and 7 have absorption maxima roughly between 300 and 350 nm in qualitative agreement with published works.^{18f,g} This transient was first reported by Nakamura et al. in a conventional flash photolysis study and identified as a ketene.¹⁵ Furthermore, it is known that ketene is a relatively stable species, i.e., long lived, and that it may undergo three types of reactions depicted in Figure 1, based on product analysis.¹⁹⁻²³ Ketene may react with hydroxy group containing solvents²¹⁻²³ (reaction 5), with a ketene¹⁹ (reaction 6), and with the parent *o*-diazo ketone²⁰ (reaction 7). In the case of DNQ-4STL and DNQ-5STL, the bimolecular reaction B + B (reaction 6) was observed, confirming its assignment to a ketene. For other DNQ's reactions 6 and 7 were not detectable. This indicates that their rates are slow compared with reaction 5, in agreement with continuous photolysis results,²¹ where 3-carboxyindenesulfonates are the main final products for 5-sulfonate analogues. The rate constants given in Table II as k_{BC} can then be assigned to k_S for the first-order kinetics and $k_{\rm K}$ for the second-order ketene-ketene reaction. Reaction 5 is of course a bimolecular reaction, but k_s is given in s⁻¹ since the solvent surrounds the ketene and does not have to diffuse to react with it. $k_{\rm S}$ is very sensitive to solvents: for DNQ-5S, DNQ-4S, and DBQ its values are orders of magnitude larger for methanol than for water as shown in Table II. Finally,

⁽¹⁷⁾ Bensasson, R.; Gramain, J. J. Chem. Soc., Faraday Trans. 1 1980, 76, 1801.

⁽¹⁸⁾ Ketenes produced through the Wolff rearrangement are spectroscopically identified. For examples, methylketene was synthesized by Arendale or Moore et al. and was identified in an argon matrix by Kranz. See: (a) Arendale, W. F.; Fletcher, W. H. J. Chem. Phys. 1957, 26, 793. (b) Moore, C. B.; Pimentel, G. C. J. Chem. Phys. 1963, 38, 2816. (c) Kranz, A. J. Chem. Soc., Chem. Commun. 1973, 670. Aromatic ketenes from diazonaphthoquinone derivatives were also identified. See: (d) Pacansky, J.; Johnson, D. J. Electrochem. Soc. 1977, 124, 862. (e) Pacansky, J.; Coufal, H. J. Am. Chem. Soc. 1980, 102, 410. (f) Hacker, N. P.; Turro, N. J. Tetrahedron Lett. 1982, 23, 1771. Groot et al., reported a stable and isolated ketene at room temperature. See: (g) Groot, de A.; Boerma, J. A.; Valk, de J.; Wynberg,

<sup>K. J. Org. Chem. 1968, 33, 4025.
K. J. Org. Chem. 1968, 33, 4025.
(19) (a) Boese, A. B., Jr. Ind. Eng. Chem. 1940, 32, 16. (b) Andreades, S.; Carlson, H. D. Org. Synth. 1973, 5, 679.
(20) (a) Wiberg, K. B.; Hutton, T. W. J. Am. Chem. Soc. 1954, 76, 5367.</sup>

⁽b) Reid, W.; Mengler, H. Ann. Chem. 1962, 651, 54. (c) Yates, P.; Robb,

E. W. J. Am. Chem. Soc. 1957, 79, 5760.
 (21) Sus, O. Ann. Chem. 1944, 556, 65

⁽²²⁾ Rodionova, G. N.; Tuchin, Y. G.; Protsenko, N. P.; Erlikh, R. D. Zh. Vses. Khim. Obshchest. **1973**, 18, 355.

⁽²³⁾ Kobalina, G. A.; Askerov, D. B.; Dyumaev, K. M. Zh. Org. Khim. 1982. 18, 456.

the observation that the reactivity of transient B is accelerated by acids also supports its assignment to a ketene. It is well documented in the literature that the reaction of dimethylketene with water and alcohols is catalyzed by acids.²⁴

The precursor to ketene, transient A, could be either a ketocarbene or an oxirene. As we have discussed before,¹⁴ if it is a ketocarbene one would expect it to react with reagents such as O₂, methanol, and acetic acid. However, this was not observed. Only the rate of transformation of A into the ketene is accelerated by methanol for the DNQ's and DBQ. Furthermore, recent theoretical computations on a model compound predict that oxirene should be a true intermediate with a potential barrier of only 8 kJ/mol to yield the corresponding ketocarbene, the latter being a transient state on the way to ketene.^{12a} The activation barriers in Table III (10-20 kJ/mol) are in amazingly close agreement with those predictions. With all the above considerations in mind, transient A can only be assigned to oxirene. k_{AB} must then correspond to either k_4 or k_{-2} in Figure 1.

In a recent report by Delaire et al.,¹³ two short-lived transients were observed for DNQ-5STL in 2-ethoxyethyl acetate but only one was observed for DNQ-5S in water. The latter corresponds to our transient B. Their interpretation is that their first transient A is a ketene and that their second transient \mathbf{B} is a ketene/water dimer hydrogen-bonded complex. Although that might be true for DNQ-5STL in 2-ethoxyethyl acetate in the presence of water, it cannot explain the results for DNQ-5S. There are several reasons for this. First, such a complex would be formed in picosecond time scales in pure water and not in 0.3 μ s as measured here. Second, if the transient spectra of ketene is changed so significantly through hydrogen bonding with water dimer (on going from A to B), then one would expect transient B in water (ketene/water dimer complex) to have a very different spectrum from transient B in methanol (ketene-methanol complex). However, that is not the case (see, for example, Figures 4 and 5).

The thermodynamic results in Table III show that the activation barriers for the conversion of oxirenes into ketenes are very small. Consequently, as has been pointed out by Lewars,^{2a} oxirenes would be expected to be very short-lived on the basis of that criteria alone.

(24) Lillford, P. J.; Satchell, D. P. N. J. Chem. Soc. B 1968, 889.

Our results show that what makes oxirene detectable in the nanosecond/microsecond time scales stems from the low preexponential factors. These are best explained by a negative entropy of activation due to the rearrangement of the solvent around the solute. Therefore, the presence of solvent molecules, which may reorganize around the diazo ketone, is a key to detection of oxirene in reasonable time scales. This probably explains the difficulty in detecting oxirenes in gas-phase experiments or low-temperature solid-matrix experiments.²⁵ The important role of the solvent in the stability of oxirene is further confirmed by the strong dependence of k_{AB} on solvent composition as shown in Figure 9. This can also be seen in thermodynamic results for DBQ in Table III: on going from pure water to pure methanol the potential barrier drops by a factor of 2 and the frequency factor decreases by nearly an order of magnitude.

Conclusion

The following have been established for six-membered ring o-diazo ketones: (i) The Wolff rearrangement is a multistep process and not a concerted mechanism. (ii) Both the thermodynamics and the reactivity indicate that the precursor to ketene is most likely an oxirene. In any case it cannot be a ketocarbene. (iii) The lifetime of oxirene is mainly controlled by solute-solvent interactions. Therefore, the choice of a right combination of solute and solvent is key to its stability and therefore its detectability.

Acknowledgment. K.T. acknowledges Drs. K. Honda and A. Yabe of the National Chemical Laboratory for Industry for affording him the use of argon isolation apparatus and for their discussions. Thanks are due to Toyo Gosei Chemical Company, where NQD's and DBQ were especially synthesized for this study. The research described herein was supported, in part, by the Office of Basic Energy Sciences of the Department of Energy.

Registry No. DNQ-55, 2657-00-3; DNQ-45, 64173-96-2; DNQ, 879-15-2; DNQ-5STL, 120410-44-8; DNQ-4STL, 120410-45-9; DBQ, 4024-72-0; DM, 7270-63-5.

Interfacial Stoichiometry of a Microemulsion System

H. L. Rosano,* A. L. Nixon,

Department of Chemistry, The City College of the City University of New York, New York 10031

and J. L. Cavallo

General Foods USA, Technical Research Center, 555 South Broadway, Tarrytown, New York 10591 (Received: January 4, 1988; In Final Form: January 6, 1989)

An o/w emulsion (4 g of sodium dodecyl sulfate (SDS); 4 mL of *n*-hexadecane $(n-C_{16})/20$ mL of H₂O) was titrated to clarity with 1-pentanol (*n*-C₅OH). When (1) *n*-C₅OH volume versus H₂O volume and (2) *n*-C₁₆ volume versus *n*-C₅OH volume were plotted, two straight lines were obtained. The microdroplet is assumed to be an interfacial sheath with a *n*-C₁₆ core and *n*-C₅OH distributed between three phases, oil, water, and the interface. The amount of *n*-C₅OH in the oil core and in the continuous phase was determined. The minimum volume of *n*-C₁₆ required to form a microemulsion was also determined. From the experiments the calculated molar interfacial stoichiometry was found to be 2 *n*-C₅OH/3.5 SDS/1 *n*-C₁₆. To substantiate the proposed model, DSC curves of frozen microemulsion containing various volumes on *n*-C₅OH were investigated. Peak temperatures were found to be *n*-C₁₆ (18.33 °C), H₂O (-2.04 °C), and the interfacial sheath of constant interfacial composition.

Introduction

Mixtures of an oil and water in the presence of a surface-active agent customarily form coarse emulsions which are generally optically opaque, or nearly so, and being unstable will usually

(1) Stoeckenius, W.; Schulman, J. H.; Prince, L. M. Kolloid-Z. 1960, 169, 170.

separate on standing. In some cases, transparent mixtures of oil

and water can be prepared with the proper combination of surface-active materials. Terms such as microemulsion,¹ swollen

⁽²⁵⁾ A recent successful attempt to observe oxirene in low-temperature (12 K) rare-gas matrix was brought to our attention. See: Debu, F.; Monnier, M.; Verlaque, P.; Davidovics, G.; Pourcin, J.; Bodot, H.; Aycard, J. P. C. R. Acad. Sci. Paris **1986**, 303, 897.

^{*} Address correspondence to this author.