TABLE IV: Diffusion Constants Derived from Eq 6, Applying Stick and Slip Boundary Conditions (D in 109 s⁻¹)

	cinnamic acid		methyl cinnamate		
	slip	stick	slip	stick	
D _{xx}	0.178	0.119	1.55	1.03	
D_{yy}^{m}	0.172	0.115	1.34	0.89	
D.,	4.790	3.200	10.0	6.67	

by spheres of different magnitude. The diagonal elements of the friction tensor are described as

$$\Xi_{\alpha\alpha} = \sum_{i} \frac{F_{\alpha} \cdot r_{i}}{\omega_{\alpha}} = \sum_{i} \frac{\nu \cdot 6\pi \cdot \eta \cdot a_{i} \omega_{\alpha} r_{i}^{2}}{\omega_{\alpha}} = \sum_{i} 6\pi a_{i} r_{i}^{2} \cdot \nu \cdot \eta = \sum_{i} \xi_{i} r_{i}^{2} \qquad \alpha = x, y, z \quad (6)$$

 ω_{α} is the angular velocity, $F_{\alpha} \cdot r_i$ is the angular momentum, ξ_i is the friction constant, η the viscosity, a_i is the magnitude of the sphere i, r_i is the distance between the atom and the axes of rotation, $\nu = 2/3$ describes the slip boundary, and $\nu = 1$ is the stick boundary condition.

Employing this formula on the dimeric cinnamic acid and methyl cinnamate, one realizes that D_{xx} and D_{zz} are within the right order of magnitude. D_{yy} , however, shows serious deviations between these and the above fitted values (Table IV).

This probably can be attributed to the fact that the system is planar and therefore the rotation around the D_{yy} axis, perpendicular to the molecular plane, is not well described. To correct this value the microviscosity (Gierer and Wirtz¹⁶) has been taken into account, using the equation

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where a_s is the radius of the solvent and a is the thickness of the planar solute. The assumption $a_s/a = 2$ leads to f = 0.083 and further to $D_{yy'} = D_{yy}/f = 2.07 \times 10^9 \text{ s}^{-1}$ which is in much better

 $f = [6a_s/a + (1 + a_s/a)^{-3}]^{-1}$

accordance. Experiments

All experiments have been performed with degassed samples. The samples were dissolved in Me_2SO-d_6 as 0.1 M solutions. The viscosities were determined as $2.616 \times 10^{-3} \text{ kg/(m s)}$ for cinnamic acid and $2.347 \times 10^{-3} \text{ kg/(m s)}$ for methyl cinnamate. The time evolution of the magnetization was measured either by the well-known inversion recovery method or by applying a proton inversion pulse followed by a ${}^{13}C$ detection pulse at different evolution times $[{}^{1}H(180^{\circ})-\tau^{-13}C(90^{\circ})-acquisition-W]n$. The waiting time W was 10 times the longest T_1 . The experimental errors are within a limit of $\pm 5\%$.

Conclusion

It has been demonstrated that for an AMX spin system the cross-correlation contributions between the spins M and X, in situations where A is a carbon atom, are significant. Furthermore, it demonstrates that investigation of the coupled relaxation allows the determination of the anisotropic rotational diffusion constants, by using a least-squares fit procedure. The diffusion coefficients as well as the random field values, which were treated in the least-squares procedure as parameters, were cross-checked by different independent measurements.

Acknowledgment. The XL 200 NMR spectrometer was put at our disposal by the "Fonds zur Forderung der wissenschaftlichen Forschung Pr.Nr. 3293" which is gratefully acknowledged.

Registry No. Cinnamic acid, 621-82-9; methyl cinnamate, 103-26-4.

Confirmation of a Large Kinetic Isotope Effect in the Low-Temperature Matrix Reaction of Diphenylcarbene with Toluene

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The reaction of diphenylcarbene with toluene was investigated as a function of temperature. The distribution of products formed in this reaction and the kinetic isotope effects observed (>100 at 77K) are consistent with a triplet carbene mechanism over a wide temperature interval. A very large kinetic isotope effect on the carbene reaction was observed in a frozen matrix of toluene-d₁ at 77 K. Kinetic isotope effects of this magnitude have not been observed in previous matrix kinetic and chemical studies. This is consistent with a previous interpretation of a matrix EPR kinetic study.

Introduction

The reaction of diphenylcarbene (DPC) with toluene has been extensively studied by physical methods. Photolysis of diphenyldiazomethane (DPDM) in toluene in the probe of an NMR spectrometer liberates DPC which subsequently reacts with solvent. The stable products formed in this reaction display strong nuclear spin polarization.² Closs' analysis of this system led to the development of the radical pair theory of CIDNP. In more recent work, Hadel, Platz, and Scaiano have measured the absolute rate of reaction of DPC with toluene by laser flash photolysis.³

For several years we have been interested in the low-temperature matrix reactions of triplet arylcarbenes with hydrogen atom donors.⁴ Brief photolysis of DPDM in frozen toluene between 77 and 100 K gave the well-known triplet EPR signal of DPC. The EPR signal decayed rapidly upon shuttering the light source due to a hydrogen atom abstraction reaction of the carbene with the matrix. Schaeffer has calculated the potential surface for reaction of triplet methylene with methane. The migrating hydrogen atom is in the plane of methylene and along the line which bisects the HCH bond angle³

(7)

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SCHEME I



The photogenerated matrix-isolated triplet arylcarbenes have only a limited range of motion available in the solid and will have difficulty achieving the optimal alignment for hydrogen transfer in the low-temperature polycrystal. The carbenes are in fact distributed in a multitude of sites in the matrix which are nonequivalent with respect to the matrix CH bonds. The triplet carbenes are created in sites with different local environments and consequently different absolute reactivities. This leads to highly complex and severely nonexponential decay of the EPR signal associated with the carbene. This type of kinetic behavior has also been observed with matrix-isolated hydrogen atoms, free radicals,⁶ and excited states.⁷ Theoretical models of the complex matrix kinetics have been advanced which justify the nonexponential decay in terms of a multiple-site distribution but to our knowledge the multiple reaction site hypothesis has not been independently verified.8

Despite the complexities caused by site inequivalence we have struggled to interpret the matrix kinetics by analyzing only the initial carbene decay.⁴ Using this approach we found a highly unusual temperature dependence of the kinetic isotope effects. The ratio of Arrhenius preexponential factors for toluene and toluene- d_8 was $A_D/A_H \approx 20.4$ This led us to postulate that atom transfer was by a quantum mechanical tunneling (QMT) mechanism. We noted, however, that the kinetic isotope effects observed by EPR at any single temperature were orders of magnitude smaller than predicted by either a classical or a QMT mechanism. This discrepancy was blamed on the multiple-site problem and the slow time resolution of our EPR experiment. We postulated that the observed values of $k_{\rm H}/k_{\rm D}$ compared "slow" sites in protic matrices with "fast" sites in deuterated matrices and were much smaller than the kinetic isotope for the same site in protic and deuterated matrices.

In this study we have used chemical analysis to ascertain the magnitude of the kinetic isotope effect on the reaction of triplet DPC with toluene in solution and in a frozen solid. The results demonstrate that the matrix kinetic isotope effects are substantially larger than those measured by EPR when freed of site complications and support the concept of a multiple-site distribution. Unfortunately we have not been able to measure the isotope effect with sufficient precision to distinguish between a classical or QMT mechanism of atom transfer.

TABLE I: Distribution of Products Found on Photolysis of Diphenyldiazomethane in Toluene-Toluene-d₈

temp, °C	1	2	3	4	5	6	total	
65 ^b	16	42	3	22	8	е	91	
26 ^b	8	20	21	11	7	5	72	
-5 ^b	10	23	17	13	5	1	69	
-50 ^b	8	29	8	16	13	d	74	
-97 ^b	5	28	1	18	17	d	69	
-146°	d	96	d	1	d	d	97	
-196°	d	100	d	d	d	d	100	
26 (O ₂) ^e	d	d	d	d	d	83	83	

^a1:1 toluene:toluene- d_8 , 1.6 × 10⁻² M diazo compound, all yields by GC using naphthalene internal standard. ^bSolution phase. ^c Polycrystal. ^d The yields were less than 1%. ^e Sample was saturated with oxygen.

Solution-Phase Reaction of DPC and Toluene

The chemistry of DPC in toluene was initially studied by Kirmse, Horner, and Hoffmann⁹ who reported the formation 1,1,2,2-tetraphenylethane, apparently by dimerization of the benzhydryl radical. Closs has found that photolysis of DPDM in toluene gives a nearly 1:2:1 mixture of 1,2-diphenylethane (1), 1,1,2-triphenylethane (2), and 1,1,2,2-tetraphenylethane (3).² This was taken as evidence for a mechanistic scheme in which triplet DPC abstracts a hydrogen to give the triplet benzyl-benzhydryl radical pair (Scheme I). Diffusive separation of the radical pair should eventually lead to a statistical distribution of the possible radical-radical coupling products 1, 2, and 3. These workers did not report the formation of head-to-tail benzylic radical dimers. In the solid state symmetric radical-radical coupling is suppressed, the near exclusive chemistry being characteristic of cage recombination (vide infra).

In our hands photolysis of DPDM in a 1:1 mixture of toluene-toluene- d_8 gave the product distribution shown in Table I. The following products were observed: 1,2-diphenylethane (1), 1,1,2-triphenylethane (2), 1,1,2,2-tetraphenylethane (3), tetraphenylethylene (5), benzophenone (6), and benzophenone azine (4). At 26 °C considerable amounts of 1, 2, and 3 are formed in a ratio which is in reasonable agreement with Closs's work. There is also a considerable amount of carbene-carbene dimer 5 produced. This is consistent with the long lifetime ($\approx 2 \mu s$) of DPC in toluene. The relatively slow reaction of DPC with solvent allows dimerization of DPC to complete with hydrogen atom abstraction. The high yield of 4 also reflects the long solution lifetime of DPC. Triplet DPC is nearly completely consumed by oxygen in an oxygen-saturated toluene solution to give an 83% yield of benzophenone. This reaction has recently been studied by laser flash photolysis.¹⁰

The large yield of the symmetric radical dimers 1 and 3 between 65 and -5 °C support a predominant if not exclusive triplet-state decay mechanism of DPC over this temperature interval. Between -50 and -97 °C the yields of the symmetric radical dimers have fallen relative to the yield of the unsymmetric coupling product 2. We do not think this necessarily reflects a changeover to singlet carbene chemistry but instead reflects a larger cage effect on geminate benzhydryl benzyl radical pair combination due to the increase in viscosity of toluene upon lowering the temperature.

The isotope effects are completely consistent with a triplet carbene mechanism. 1,2-Diphenylethane (1) gives a strong molecular ion from which the data were obtained. In solution phase the isotope effect is simply the ratio of $1-d_0:1-d_7$. The isotope

C ₆ H ₅ CH ₂ CH ₂ C ₆ H ₅	C ₆ D ₅ CD ₂ CH ₂ C ₆ H ₅
$1-d_0$	$1-d_7$
M ₁₈₂	M ₁₈₉

effect of 7.0 is near the maximum possible at 25 °C in the absence of tunneling. The value obtained by chemical analysis in this work is in excellent agreement with the laser spectroscopic value of 6.5

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measured by Hadel.³ A plot of $\ln (k_H/k_D)$ vs. 1/T gives a straight line from which it was determined that $E_a(D) - E_a(H) = 1.4$ kcal/mol. This means the transition state is highly symmetric and probably linear with complete loss of ground-state CH(D) stretching zero point energy. The large isotope effects are completely consistent with a pure triplet-state reaction of DPC. The ratio of preexponential factors $A_H/A_D = 0.62$ does not support an important tunneling contribution to the solution-phase reaction.¹¹

Analysis of the GC-MS of 2 also supports a triplet mechanism. The asymmetric coupling product 2 can be shown to originate from the benzyl-benzhydryl radical pair by isotopic labeling. Insertion of singlet DPC into a benzylic C-H(D) bond of toluene (toluene- d_8) will give only 2- d_0 and 2- d_8 (Scheme II). The reaction of triplet DPC with solvent will give a triplet radical pair which can suffer diffusive separation rather than collapse. This will lead to the eventual formation of radical crossover products 2- d_1 (M₂₅₉) and 2- d_7 (M₂₆₅) as well as the 2- d_0 and 2- d_8 products. The ratio

$$(C_6H_5)_2CDCH_2C_6H_5 \qquad (C_6H_5)_2CHCD_2C_6D_5$$

2-d 2-d₇

of $M_{258}:M_{259}$ (M:M + 1) for pure 2- d_0 is 100:15. The ratio in solution at 65 °C is nearly twice this amount, 100:28, indicating a substantial amount of 2- d_1 . Similarly the ratio of $M_{265}:M_{266}$ (M - 1:M) of pure 2- d_8 (obtained by reaction of DPC with toluene- d_8 at -196 °C) is 1:10. At 65 °C the ratio is 9:3, indicating a substantial amount of the other crossover product 2- d_7 . Thus the chemistry of DPC in toluene strongly supports the concept of a largely triplet reaction which is in accord with previous interpretations.^{2,3,9}

Matrix Reaction of DPC and Toluene

The chemistry of DPC in polycrystalline 1:1 (v/v) toluenetoluene- d_8 was examined at -140 and -196 °C. In the matrix the yields of 1,1,2-triphenylethane (2) were 96 and 100% respectively at the aformentioned temperatures. The geminate benzhydryl-benzyl radical pair cannot diffuse apart in the polycrystal hence radical-radical coupling is extremely efficient. We attempted to measure matrix isotope effects from the ratio of $2-d_0$ (M₂₅₈): $2-d_8$ (M₂₆₆) (Table III). If one assumes that cage collapse of the benzyl-benzhydryl pair is 100% efficient in the solid state than the isotope effect is simply $k_{\rm H}/k_{\rm D} = [2-d_0]/[2-d_8]$. The values obtained at -146 and -196 °C are 6.3 and 10, respectively. The molecular ion for 2 is much less intense than that of 1, resulting

TABLE II: Solution-Phase Isotope Effects for the Reaction of DPC with Toluene-Toluene- d_8 As Monitored by GC-MS of 1.2-Diphenvlethane^a

 temp, °C	$1 - d_0 (M_{182})$	$1-d_7 (M_{189})$	$k_{\rm H}/k_{\rm D}$	
25	10.93	1.56	7.0	
-6	10.64	1.09	9.8	
-50	10.68	0.80	13	
-98	11.71	0.28	42	

^{*a*} 1:1 toluene:toluene-*d*₈. Diazo concentration was 1.6×10^{-2} M.

TABLE III: GC-MS of 1,1,2-Triphenylethane (2) and Its Deuterated Modifications from Reaction of DPC with Toluene-Toluene- d_8^a

temp, °C	M ₂₅₈	M ₂₅₉	M ₂₆₅	M ₂₆₆	$k_{ m H}/k_{ m D}$	
65 ^b	100	28	9	3		
26 ^b	100	22	5	d		
5 ^b	100	24	4	1		
-50 ^b	100	21	3	d		
-97 ^b	100	20	1	d		
-140^{c}	100	19	1	16	6.3	
-196 ^c	100	15	2	10	10	

^a1:1 toluene-toluene- d_{s} ; diazo concentration was 1.6×10^{-2} M. ^bSolution phase. ^cPolycrystal. ^dToo small to measure.



Figure 1. Deuterium NMR of 1,1,2 triphenylethane obtained on photolysis of diphenyldiazomethane in (a) toluene- d_1 and (b) toluene- d_3 at 77 K.

in decreased precision, but it is clear that the matrix isotope effects are much smaller than those observed in solution. In the absence of a "matrix effect" there should not be a sharp break in a plot of ln $(k_{\rm H}/k_{\rm D})$ vs. 1/T. A change in mechanism from triplet to singlet DPC with temperature would still show a smooth linear progression. A change in mechanism of the reaction with solvent from ground-state triplet to singlet DPC upon freezing the toluene solution is contrary to a substantial body of matrix carbene chemistry. We attribute the small matrix isotope effects observed in toluene-toluene- d_8 to the rigidity of the matrix which limits the range of motion of triplet DPC in the solid state. Under these conditions the proximity of triplet DPC to a CH(D) bond is as important as the isotopic mass in determining whether reaction occurs with a CH or CD bond. As the distribution of DPC with respect to toluene or toluene- d_8 is probably very similar the apparent isotope effect is greatly reduced. There are very few sites where DPC has sufficient mobility to choose between H or D atom abstraction.

The matrix chemistry of DPC was studied next in toluene- d_1 . We hoped that there was sufficient mobility in the matrix to allow triplet DPC to distinguish between H vs. D atoms bound to the same benzlyic carbon. The D atom NMR spectrum of $2-d_1$ obtained from reaction is shown in Figure 1 along with the spectrum of $2-d_8$ (obtained from reaction with toluene- d_8). The product of deuterium atom transfer (A) cannot be detected; the

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Figure 2. The deuterium NMR of 9-benzylfluorene obtained on photolysis of 9-diazofluorene in (a) toluene- d_1 and (b) toluene- d_8 at 77 K.

only product observed is that of H atom abstraction-recombination (B). A conservative lower limit of the isotope effect at -196 °C



is 100! Similar results were obtained in the reactions of fluorenylidene (Fl) with toluene- d_1 at -196 °C (Figure 2). In a toluene- d_1 matrix at 77 K ³DPC and ³Fl can undergo competitive reactions with CH and CD bonds with a minimum of interference by the matrix, hence a more representative isotope effect is observed.

Conclusions

Asymmetric Eckart barrier calculations of the reaction of ³DPC with toluene (toluene- d_8) at 77 K predict a kinetic isotope effect of 10⁴ at this temperature.^{4,8,11} The isotope effect predicted at 77 K for DPC for a classical hydrogen atom transfer (from the solution-phase Arrhenius data) is also very large, 5.5×10^3 . The kinetic isotope effect measured in this work for the reaction of DPC with toluene is greater than 100. The precision of the experimental data prevents us from determining values as large as those predicted from QMT theory or solution-phase work. It certainly does not allow us to distinguish classical vs. quantum mechanical atom transfer. In the absence of matrix site problems the kinetic isotope effects determined by EPR for the decay of ³DPC and ³Fl in toluene and in toluene- d_8 and the chemically measured isotope effects for ³DPC in a 1:1 mixture of toluene and toluene- d_8 should be in excess of 100. The fact that the chemically determined isotope effects are at least 10 times less than this value indicates that matrix-isolated carbenes cannot freely distinguish CH and CD bonds in the frozen matrix. The fact that the isotope effects determined for the rate of decay of ³DPC and ³Fl in toluene and in toluene- d_8 at 77 K are very much lower than the present toluene- d_1 study proves that the EPR method is not comparing carbenes in equivalent sites in toluene and toluene- d_8 with respect to atom transfer. This provides independent support of the multiple reaction site hypothesis proposed earlier workers.

Experimental Section

Photolyses were performed with two Rayonet RPR-3500 bulbs in 5-mm Pyrex tubes prewashed with ammonia. Products were analyzed with a Hewlett Packard 5830 gas chromatograph using a 6 ft by 1/4 in. 10% SE-30 column. Compounds were identified

on the basis of coinjection with known compounds and GC-MS. Preparation of α -Deuteriotoluene. A solution of benzylmagnesium chloride in tetrahydrofuran (Alfa, 1:5 M solution, 67 mL) was syphoned under nitrogen into a 250-mL two-necked round-bottomed flask fitted with a reflux condenser and carrying a drying tube on one neck and a rubber septum on the other. The reaction flask with its contents was continuously swept by dry nitrogen. The solution was stirred by a small magnetic bar and cooled in ice-water while methyl alcohol-O-D (Aldrich, 99.5 atom % D, 6 mL) was introduced dropwise through the rubber septum by means of an injection syringe. The reaction mixture was allowed to warm to room temperature and portioned between dichloromethane (50 mL) and water (50 mL). The organic layer was separated and the aqueous layer extracted with dichloromethane (2 \times 20 mL). The combined organic extracts were dried (anhydrous $MgSO_4$) and distilled with a fractionating column. The fraction boiling between 109 and 112 °C was collected and redistilled yielding 6.2 (67%) of colorless liquid boiling at 111-112 °C

¹H NMR (CDCl₃): δ 2.3 (s, 2 H), 7.2 (s, 5 H). In the ¹³C NMR the carbon signal due to CH₂D was split into a triplet due to the presence of deuterium. Accurate mass measurement gave a top mass peak at 93.0688.

Irradiation of Diphenyldiazomethane/9-Diazofluorene in α -Deuteriotoluene (General Procedure): A solution of diphenyldiazomethane (or 9-diazofluorene) (2 \times 10⁻² M) in α deuteriotoluene (500 µL) was taken in a previously washed (ammonium hydroxide) and dried (110 °C) Pyrex tube. To maximize the surface area, a glass rod was inserted into the tube. The sample was degassed by three freeze-pump-thaw cycles and sealed. The tube was then suspended in liquid nitrogen and photolyzed for 40 h with four Rayonet lamps (RPR 3500). After 10 h of photolysis at liquid nitrogen temperature, the reaction mixture was kept at 77 K for 14 to 16 h. The solvent was evaporated at room temperature and chromatographed over basic alumina in hexane. Elution with 1:1 pentane:hexane furnished a waxy solid. The solid was dissolved in dry chloroform and the solution was used to record the 500-MHz D NMR. 500 MHz D NMR (CHCl₃): δ 3.3703 (s, 1 D, Ph₂CH-CHDPh).

A control experiment was done under identical conditions using toluene- d_8 . The product obtained was purified as above and deuterium NMR recorded; 500 MHz D NMR (CHCl₃): δ 3.3810 (s, 2 D, Ph₂CD-CD₂Ph); 4.2464 (s, 1 D, Ph₂CDCD₂Ph).

Identical conditions and product work-up procedures were employed for 9-diazofluorene with α -deuteriotoluene and toluene- d_8 as with diphenyldiazomethane.

9-Diazofluorene with α -Deutriotoluene. 500 MHz D NMR (CHCl₃ + CDCl₃): δ 3.1197 (s, 1 D, 9Fl-C-CHDPh).

9-Diazofluorene with Toluene- d_8 . 500 MHz D NMR (CHCl₃ + CDCl₃): δ 3.12 (s, 2 D, 9Fl-CD-CD₂Ph); 4.274 (s, 1 D, 9Fl-CD-CD₂Ph).

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Appendix

The reaction of DPC with toluene and toluene- d_8 proceeds with rate constants $k_{\rm H}$ and $k_{\rm D}$, respectively.

$$Ph_2C + C_6H_5CH_3 \rightarrow Ph_2CH + C_6H_5CH_2 \qquad k_H \qquad (1)$$

$$Ph_2C + C_6D_5CD_3 \rightarrow Ph_2CD + C_6D_5CD_2 \qquad k_D \qquad (2)$$

The isotope effect is then

$$k_{\rm H}/k_{\rm D} = [C_6 H_5 C H_2] / [C_6 D_5 C D_2]$$
 (3)

when $[C_6H_5CH_3] = [C_6D_5CD_3]$. The relative yield of $C_6H_5C-H_2CH_2C_6H_5$ and $C_6H_5CH_2CD_2C_6D_5$ is given by

$$\frac{[C_6H_5CH_2CH_2C_6H_5]}{[C_6H_5CH_2CD_2C_6D_5]} = \frac{k[C_6H_5CH_2]^2}{k[C_6H_5CH_2][C_6H_5CD_2]}$$
(4)

where k is the rate constant for radical-radical recombination. It is assumed that the secondary isotope effect for radical dimerization is unity. Combining eq 3 and 4 yields

$$k_{\rm H}/k_{\rm D} = [C_6H_5CH_2CH_2C_6H_5]/[C_6H_5CH_2CD_2C_6D_5]$$
 (5)

The square of the isotope effect is given by

$$(k_{\rm H}/k_{\rm D})^2 = [C_6H_5CH_2CH_2C_6H_5] / [C_6D_5CD_2CD_2C_6D_5]$$
(6)

The same relationship will hold in the triphenyl- and tetraphenylethane series.

$$k_{\rm H}/k_{\rm D} = [Ph_2CHCH_2C_6H_5]/[Ph_2CDCH_2C_6H_5] = [Ph_2CHCHPh_2]/[Ph_2CDCHPh_2] (7)$$

It is more precise to measure the isotope effect using (5) rather than (7) as the mass difference is only 1 unit in the latter ions and must be corrected for the natural M + 1 peaks. An even more serious problem in the use of (7) is that the requisite molecular ions are very small.

Registry No. 1, 103-29-7; 2, 1520-42-9; 3, 632-50-8; 4, 983-79-9; 5, 632-51-9; 6, 119-61-9; DPC, 3129-17-7; Fl, 2762-16-5; D₂, 7782-39-0; toluene, 108-88-3; diphenyldiazomethane, 883-40-9; benzyl chloride, 100-44-7; α-deuteriotoluene, 1861-00-3; 9-diazofluorene, 832-80-4.

Thermochemical Bistability in an Illuminated Liquid-Phase Reaction

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The acid-base reaction of o-cresolphthalein (OCP) in a buffered aqueous solution held at a given bath temperature has thermochemical bistability when driven far from equilibrium with light. The phenomenon is observed in a cell in which the entire liquid volume is exposed to light (closed to mass flow) and a cell in which only a small fraction of the liquid volume is illuminated (open). The driving laser radiation (514.5 nm) is absorbed only by the basic form of the molecule. Theoretical results correctly predict the dependence of the bistable region on the pH of the solution and the bath temperature. The enthalpy of reaction for the deprotonation of OCP is determined to be $29.9 \pm 3.0 \text{ kJ/mol}$. The quantum yield for the photodissociation of the basic form of OCP at 514.5 nm is measured to be $4 \times 10^{-6} (\pm 50\%)$.

I. Introduction

Bistability has been exhibited in chemical systems, with certain types of feedback, maintained far from equilibrium.¹⁻³ Chemical systems with bistability have been studied mostly in continuously stirred tank reactors,⁴ but the phenomenon may be observed when a chemical system is driven far from equilibrium with light.^{5,6} In these experiments, the system has been a gas-phase dimerization reaction in which the feedback results from differential absorption; only the monomer, which is favored at high temperature, absorbs the radiation.

We report here the first measurements on bistability in an illuminated thermochemical liquid-phase system: the acid-base reaction of o-cresolphthalein (OCP) in a buffered aqueous solution. This system is predicted to exhibit the bistability when illuminated with radiation absorbed only by the basic form of the molecule. Bistability is observed and the dependence of the resulting hysteresis loop on external parameters is investigated theoretically and experimentally. The experiments are particularly simple and yield the first observation of bistability in a system absolutely closed to mass flow.

In section II we present the essential theory of the OCP system and multiple stationary states, bistability, and hysteresis are predicted from simple model equations. Under appropriate

TABLE I: Parameters Used in Eq 2 and 3

para- meter	definition	units	value
X ₀	total concentration of OCP species	mol/cm ³	8.7×10^{-7}
С	heat capacity of irradiated region	J/K	4.32×10^{-5}
ε	extinction coefficient of OCP ⁻ at 514.5 nm	cm ² /mol	4.2×10^{7}
β	thermal diffusivity	W/K	1.2×10^{-3}
ΔH	enthalpy change of reaction	kJ/mol	29.9 ± 3.0
Р	incident laser power	W	0-0.3
1	cell path length	cm	0.2
T_0	bath temperature	K	292-333
k_2	recombination rate coefficient	$cm^3/(mol s)$	5×10^{17}
R	gas constant	J/(mol K)	8.025
a'	preexponential factor	mol/cm ³	2.3×10^{-9}
A	absorption	dimensionless	0-1
V	irradiated volume	cm ³	1.27×10^{-5}
r	$1/e^2$ intensity radius	cm	4.5×10^{-3}

constraints, there are three branches of steady states; the upper and lower absorption branches are stable while the intermediate absorption branch is unstable. We calculate the dependence of these states on pH and bath temperature. The apparatus and experimental methods are described in section III. Experimental results, including measurement of the enthalpy of reaction for the deprotonation of OCP, are presented in section IV. We observe hysteresis in both a closed cell and an experimental arrangement in which slow convective flow of mass between the illuminated and nonilluminated regions is permitted. In the second case, hysteresis loops are measured for various values of pH and bath temperature, which compare well with theory. We conclude in section V with a discussion and summary of the work. An Appendix of the photodissociation of OCP⁻ completes the paper. Measurements of transitions between stationary states and the critical slowing down in this system will be presented elsewhere.⁷

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