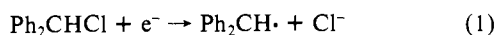


per pulse) through reaction 1.¹³ A frequency-doubled ruby laser



($\lambda_{\text{exc}} = 347 \text{ nm}$, $\sim 15 \text{ ns}$, $\sim 30 \text{ mJ/pulse}$) synchronized with the radical-producing linac pulse (typically 4- μs delay) was used to excite the radicals. The electron beam, the laser beam, and the analyzing light were all focused onto a 1-cm cell and were all perpendicular to one another. A similar setup has been previously utilized in the study of the ketyl radicals.¹⁰ Blanks were checked to ensure that all the observations described below originate from the radicals and not from the parent molecules.

The sequence of events, starting with the production of diphenylmethyl radicals in acetonitrile, is shown in Figure 1 for three different wavelengths. The lifetimes for the recovery of the ground state (Figure 1a), the decay rate of the absorption of the excited states (Figure 1b), and the fluorescence lifetime (Figure 1c) are all the same within experimental error, $\tau_f = 280 \pm 30 \text{ ns}$. All three modes display single exponential behavior. The fluorescence lifetime of the diphenylmethyl radical is slightly longer lived at 77 K (440 ns in EtOH matrix^{6a}) than found in this study. The long lifetime of the excited state of the benzyl-type radicals has been attributed to the low oscillator strength of the symmetry-allowed ${}^2A_2 \leftarrow {}^2B_2$ transition. It should be noted that no new absorption band could be observed at the end of the decay of the excited state of the radical in CH_3CN .

The fluorescence spectrum of the excited $\text{Ph}_2\text{CH}\cdot$ radical is shown in Figure 2a (dashed curve). This could be compared with the fluorescence spectra obtained at 77 K.¹⁴ Although the spectrum at room temperature is not as richly structured as in the glassy matrix,^{14b} vibrational structure is clearly observable. The higher energy peak, which probably corresponds to the O—O transition of the first excited doublet,^{14b} is at 19048 cm^{-1} (2.38 eV) above the ground state. The vibrational frequency of 610 cm^{-1} is probably a C—C bending mode. Using $\text{Ru}(\text{bpy})_3^{2+*}$ as a fluorescence actinometer ($\phi_{\text{em}} = 0.042$)¹⁵ we estimate the quantum yield for fluorescence of the radical as $\phi_{\text{em}} \sim 0.3$, and thus the radiative lifetime is $1.1 \mu\text{s}$.¹⁷ This estimate also implies that the quantum yield for fluorescence at 77 K is ~ 0.5 .

Assuming that the excited state of the radical absorbs negligibly at $\lambda_{\text{max}} = 330 \pm 3 \text{ nm}$ of its ground state,¹⁸ we can, for the first time, obtain the doublet-doublet absorption spectrum of the excited state. This spectrum is shown in Figure 2b. With the above mentioned assumption, one can estimate the extinction coefficients for the absorption of the first excited state of the radical. Taking for the ground state $\epsilon_{330} = 4.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, one obtains $\epsilon_{355}^* = 3.0 \times 10^4$, obviously allowed transitions of large oscillator strength. The structure obtained in the 400–440-nm region ($\lambda_{\text{max}} = 403, 417, 435 \text{ nm}$) consistently appears in repetitive spectra measurements. We cannot at present offer a decisive result to indicate whether this is vibrational structure or actually different electronic excitations. The lowest band presently observed for these excitations is situated at 5.25 eV above the ground state and thus would correspond to electronic excitations to the eighth or

higher levels above the ground state.^{6e}

Excitation of the triphenylmethyl radical yields dramatically different results. No emission from an excited state of this radical could be observed in EtOH, CH_3CN , or cyclohexane solutions at room temperature (compare to fluorescence lifetime of 280 ns in EtOH at 77 K^{6a}). On the other hand, high quantum yields ($\Phi \sim 1.0$) of permanent (within the lifetime of the radical) bleaching of the parent radical and rather strongly absorbing transient species ($\lambda_{\text{max}} \approx 490 \text{ nm}$, $\epsilon \sim 12\,500 \text{ M}^{-1} \text{ cm}^{-1}$) could be observed. Positive identification of this product still awaits further experiments, but several conceivable routes for the photochemical reaction could be eliminated. No long-lived (on the time scale of tens of milliseconds) excited state is expected for this radical. Photoionization of the radical is rejected since an ejected electron would immediately produce back the parent radical in the systems studied. The fact that products similar to those produced in cyclohexane and CH_3CN are produced in EtOH (and their lifetime is independent of the concentration of alcohol in the other solvents) eliminates the possibility of homolytic bond scission to form a phenyl radical and a diphenylmethylene carbene. Also the similarity of the results in the different solvents makes participation of the solvent in the initial photochemical step rather unlikely. We, therefore, tentatively favor an internal geometric isomerization as the major photochemical route for the triphenylmethyl radical. Inter-ring photocyclization similar to the one observed in related systems¹⁶ is one such pathway. Further identification of the photochemical product and the reasons for such pronounced differences between the two seemingly similar radicals are currently under investigation.

Acknowledgment. We are thankful to D. Ficht and G. Cox for their dedicated operation of the ANL linac system.

Registry No. Diphenylmethyl, 4471-17-4; triphenylmethyl, 2216-49-1.

Reactions at Phase Boundaries Using Immobilized Hydrophobic Monolayers¹

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Biphase reactions involving hydrophobic substrates and water-soluble reagents are generally slow, if there exist solubility problems of the reactants. Such reactions can be facilitated by the use of phase-transfer catalysts² or surface-active agents,³ although not many reactions proceed at appreciable rates at the liquid-liquid interface in spite of the attentions.⁴ We report here

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(17) The determination of the fluorescence quantum yield should be considered only as a rough estimate since all fluorescence spectra measured in this study are uncorrected for changes in detector sensitivity as a function of wavelength.

(18) This assumption seems reasonable in view of the correspondence of the spectrum after the laser flash with that of the narrow band of the ground-state radical in the region 310–335 nm. Furthermore with this assumption we obtain the expected quantum yield of excitation of the radical $\Phi_{\text{exc}} = 1.05 \pm 0.1$ from the bleaching of the ground state at 330 nm.

(1) The financial support by a grant from the Ministry of Education is gratefully acknowledged.

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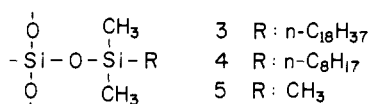
(4) (a) Menger, F. M. *J. Am. Chem. Soc.* **1970**, *92*, 5965–5971; (b) *Chem. Soc. Rev.* **1972**, *1*, 229–240. (c) Tomita, A.; Ebina, N.; Tamai, Y. *J. Am. Chem. Soc.* **1977**, *99*, 5725–5728. (d) Regen, S. L.; Besse, J. *J. Ibid.* **1978**, *100*, 7117–7119; **1980**, *102*, 7619. Most successful interfacial reactions have been observed between organic substrates in liquid phase and reagents in solid phase under ultrasonication or in the presence of inorganic supports. See, for example: Quici, S.; Regen, S. L. *J. Org. Chem.* **1979**, *44*, 3436–3437. Regen, S. L.; Quici, S.; Ryan, M. D. *J. Am. Chem. Soc.* **1979**, *101*, 7629–7630. Regen, S. L.; Singh, A. *J. Org. Chem.* **1982**, *47*, 1587–1588. Ando, T.; Kawate, T.; Yamawaki, J.; Hanafusa, T. *Chem. Lett.* **1982**, 935–938. Boudjouk, P.; Han, B.-H.; Anderson, K. R. *J. Am. Chem. Soc.* **1982**, *104*, 4992–4993 and references cited.

Table I. Reactions of Alkyl Halides at Phase Boundaries (70 °C)

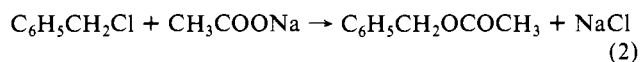
reaction	organic phase ^a	substrate charged, mmol	$10^5 k, ^b \text{ s}^{-1}$	product selectivity ^c	conversion/reaction time, h
1	3	1.15 (0.19)	13.5 (55.4) ^d	100	88/5
1	4	0.99 (0.10)	24.6 (58.2) ^d	100	98/5
1	5	0.42 (0.04)	34.0 (0.87) ^{d,e}	100	100/5 (78/48) ^{d,e}
1	3	1.17	36.7 ^f	100 ^f	98/5 ^f
1	<i>n</i> -C ₈ H ₁₇ Br ^g		0.029	100	2.5/24
2	3	0.13	4.48	81.7	91/15
2	4	0.12	6.19	80.6	96/15
2	5	0.07	13.6	80.1	94/5
2	3	0.13	9.55 ^h	90.2 ^h	81/5 ^h
2	<i>n</i> -C ₈ H ₁₈ ⁱ		0.620 (1.90) ^j	72.1 (71.3) ^j	9.1/6
2	C ₆ H ₅ CH ₃ ⁱ		0.197 (0.530) ^j	70.4 (71.5) ^j	3.1/6

^a Surface concentrations of alkylsilyl groups were 3.0×10^{-6} , 3.3×10^{-6} , and 4.2×10^{-6} mol/m² for 3, 4, and 5, respectively, based on elemental analysis. ^b Pseudo-first-order rate constants based on the disappearance of the substrate. The material balance was always better than 100 ± 2%. ^c Benzyl alcohol was produced as a byproduct from 2. ^d At reduced initial substrate concentrations shown at the left in the parentheses. ^e At room temperature without applied pressure. ^f In the presence of 0.049 mmol of tetra-*n*-butylammonium bromide. ^g Reaction between 2 mL of 1 and 20 mL of 4.0 M aqueous NaI at 1180 rpm. ^h In the presence of 0.17 mmol of tetra-*n*-butylammonium chloride. ⁱ Reaction between 12 mmol of 2 in 20 mL of the organic phase and 20 mL of 2.7 M aqueous sodium acetate adjusted to pH 5.9 at 1180 rpm. ^j 10 mL of the organic phase and 30 mL of the aqueous phase were used.

Scheme I



the study on the rapid reactions at phase boundaries between an aqueous nucleophile, sodium iodide or sodium acetate, and an alkyl halide, *n*-octyl bromide (1) or benzyl chloride (2), bound by hydrophobic interactions to monolayers of less than 2.5 nm in thickness immobilized on silica surfaces. These typical nucleophilic displacement reactions proceeded at the phase boundary up to 3 orders of magnitude faster than the conventional liquid-liquid biphasic reactions.



Alkylsilylated silica gel has been widely used in reversed-phase liquid chromatography.⁵ The binding of organic compounds to the alkylsilyl groups of the stationary phase is primarily governed by hydrophobic interactions,⁶ which are of much importance in many chemical and biochemical processes involving micelles, biomembranes, and enzymes. Thus the interfacial reactions of the bound substrates seem to be extremely interesting, since many reactions in nature are interfacial.

The stationary phases 3-5 (Scheme I), prepared as previously described⁷ by using silica particles of 15 to 30 μm in diameter and with surface areas of ca. 330 m²/g, were packed into stainless steel tubings of 4.6-mm i.d. and 10 cm in length. A substrate was charged at 25 °C onto the immobilized organic phase by passing 20 mL of 0.020-0.10 M substrate solution in 70% or 75% aqueous acetonitrile followed by a wash with 20 mL of water.⁸ Water was then replaced with the aqueous reagent solution by passing 20 mL of 2.7 M sodium acetate adjusted to pH 5.9 or 4.0 M sodium iodide through the column. After the reaction in a thermostated bath,⁹ the reaction components were recovered with

20 mL of methanol and analyzed by HPLC. Pseudo-first-order kinetics was observed with excellent reproducibility. The results are summarized in Table I.

The halogen exchange reactions of 1 bound to the immobilized organic phase 3-5 were up to a few thousand times as fast as the conventional liquid-liquid biphasic reaction run with the neat substrate as the organic phase at 1180 rpm. Without mixing, the reactions using the immobilized organic phase gave high yields comparable to those reported in phase-transfer-catalyzed reactions.¹⁰ In the case of the reaction 2, the use of the present system resulted in faster reactions and more benzyl acetate production than the corresponding liquid-liquid biphasic reactions. While the stationary phases with smaller alkyl groups resulted in faster reactions, they gave lower yields of benzyl acetate partly due to the increase in the contribution of the concurrent reaction in the aqueous phase.¹¹ The effectiveness of catalysts was much less than in phase-transfer-catalyzed reactions.

The better product selectivity with the greater reaction rates seen with 2 on 3-5 than in the liquid-liquid biphasic system and the high reactivity of alkyl bromides including *n*-tetradecyl bromide, much more hydrophobic than 1, in the halogen exchange reaction¹² strongly suggest that the rapid nucleophilic displacement reactions are taking place at the interface.

The following example will show some of the features of the present reaction system: 0.1 mmol of 1 was injected into the column packed with 5 in the stream of 4.0 M NaI at 70 °C followed by a rapid flush with 0.5 mL of methanol to spread the substrate over the surface of the stationary phase.¹³ After 2 h, the product was recovered in 97% yield with 3 mL of methanol, which resulted in droplets of the product by the introduction into water. The reaction of 1 on 5 at room temperature shown in Table I also indicates the unusually high efficiency of the present system in spite of the heterogeneity of the reaction conditions.

(9) Bubble formation in the reaction column was suppressed by applying a pressure of 50 kg/cm² in all esterification reactions, 100 kg/cm² in halogen exchange on 3 and 5, and 220 kg/cm² on 4. The rates of halogen exchange reactions were low and irreproducible under lower pressures.

(10) Reference 2b, pp 112-125.

(11) Relatively rapid liquid-liquid biphasic reactions were observed with 2 using *n*-octane as the organic solvent, while the use of toluene gave much lower rates. The reaction rate was independent of the stirring rate above 450 rpm and roughly proportional to the volume ratio between the aqueous phase and the organic phase with a minor change in the product ratio. These facts suggest that the reaction of 2 in the liquid-liquid biphasic system mainly took place in the aqueous phase, which would also be involved in the column reactions.

(12) The reaction of *n*-tetradecyl bromide (0.31 mmol on 3) with sodium iodide gave the rate constant of $3.20 \times 10^{-4} \text{ s}^{-1}$ at 70 °C.

(13) The possibility of homogeneous reactions can be ruled out from the results obtained by doing this process in water in the absence of NaI. After the methanol flush, the flow of the aqueous phase was maintained at 0.1 mL/min, but it was not necessary for the reaction to proceed.

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(8) The stainless steel columns hold 0.89 and 0.72 g of the alkylsilylated silica particles and 1.09 and 1.26 mL of the aqueous phase with the stationary phase 3 and 5, respectively. The application of 20 mL of substrate or reagent solutions ensured the equilibration of the system.

The efficiency of the present system in terms of the yield in the halogen exchange reaction was comparable to that of the phase-transfer reactions using low molecular weight catalysts¹⁰ and generally higher than that of triphase reactions using insoluble polymer catalysts.¹⁴ The present system has some similarity in appearance with triphase systems but showed much higher efficiency. Most of the triphase reactions required vigorous agitation and reaction temperatures 20–40 °C higher than the present case to produce similar yields,¹⁴ because of the slow diffusion involved with insoluble polymer catalysts.

As shown above, the present system has advantages that it needs neither a catalyst nor stirring during the reaction, in addition to the features found with triphase catalyzed reactions. The results suggest the possibility of synthetic use of the interfacial reactions which have been believed to be very slow. In addition to this, it may become possible to measure the reactivity of water-insoluble substrates in contact with aqueous reagent solutions without diffusion problems. This is in clear contrast with other reaction systems under homogeneous, phase-transfer-catalyzed, and triphase catalyzed conditions, where the actual reacting species do not react across the phase boundary between the aqueous phase and the organic phase. Although there are very few data available for comparative purposes in this respect,¹⁵ the rate constants in Table I indicate the unexpectedly high reactivity of the molecules placed at the phase boundaries.

Further studies are currently in progress on the mechanism of the reactions along with the synthetic applications of the present reaction system.

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(15) There were very few cases that measured the rates of truly interfacial reactions without diffusion problems.^{4d}

Encapsulation and Electronic Effects in a Thin-Film Model of a Rhodium–Titania Strong Metal–Support Interaction Catalyst[†]

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Active debate has recently centered on systems that exhibit strong metal–support interactions (SMSI).^{1–7} These interactions are generally diagnosed by suppressed H₂ chemisorption. The proposed explanations include encapsulation of the metal by the support^{6,7} and charge transfer from the support to the metal.^{8–10}

[†] Supported in part by the Office of Naval Research.

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We have constructed thin-film model catalysts under controlled conditions in order to study the interactions between the support and the metal. Here we present preliminary results for the Rh/TiO₂ system studied using static secondary ion mass spectroscopy (SSIMS), thermal desorption spectroscopy (TDS), and Auger electron spectroscopy (AES).

The model consists of an oxidized Ti(0001) single crystal onto which controlled amounts of Rh were vapor deposited. The Ti(0001) was oxidized in vacuum at 775 K in 5×10^{-7} torr of O₂ for 20 min. This produced a TiO₂ film approximately 20 Å thick. Underlying the TiO₂ is another region of about 30 Å of oxygen-rich Ti (TiO_x, $x < 2$). The characterization of the oxide film is based on the AES line shapes of the Ti transitions, which are correlated with previous X-ray photoelectron spectroscopy (XPS) work.^{5,11} The Rh overlayer was deposited with the oxide layer at room temperature, and its thickness was estimated from the attenuation of the substrate Ti and O AES signals. Assuming layered growth of the overlayer, we calculate the Rh thickness to be 30 ± 10 Å.¹² The quoted uncertainty accounts for the possibility of some nonuniform growth and for the very small substrate signals detectable at this thickness of Rh. To obtain a more uniform overlayer, the deposited Rh was annealed in vacuum to 625 K for 1 min during which small Ti and O AES signals appeared. These were sputtered away with a 1-KV and 100-nA Ar⁺ beam. The sample was then annealed again at 625 K for 1 min. Neither the Ti nor the O signal reappeared; this is referred to as the clean surface.

The clean surface was dosed with 10 L of H₂ at 130 K and TDS (10 K/s to 450 K) performed to obtain the hydrogen uptake. The desorption maximum was at 280 K with a half-width of 100 K. The clean surface was further characterized with AES and SSIMS. Before TDS, AES showed no detectable Ti or O, while SSIMS detected a Ti/Rh ratio of 7.6. This result reveals the excellent sensitivity of SSIMS are compared, under these conditions, to AES. This ability to detect very small concentrations coupled with its excellent surface sensitivity makes SSIMS an excellent technique for this type of study.

Following characterization of the clean surface, the sample was heated at 1 K/s to 775 K and maintained at that temperature for 8 min. Depth profiling experiments show that the TiO₂ layer remains intact throughout the annealing process. Subsequent TDS of 10 L of H₂ adsorbed at 130 K was 75% lower than for the clean surface (see Figure 1). In addition to the decrease in H₂ uptake, an increase in the Ti/Rh ratio, as measured by SSIMS and AES, was observed. There was a concurrent increase in the O/Rh AES ratio; however, the O/Ti ratio was about one-half that of TiO₂. Moreover, the line shapes of the Ti AES peaks were indicative of reduced titanium oxide.

Figure 1 shows SSIMS, AES, and TDS signals as a function of the integrated sputtering current during a depth profile of the sample that was annealed to 775 K. It was sputtered with a 1-KV and 100-nA Ar⁺ beam. After each sputtering interval and before taking the SSIMS, AES, and TDS data, the sample was reannealed to 525 K to facilitate removal of surface roughness caused by the sputtering. Great care was taken to assure that changes in effective Rh surface area were not responsible for the increases in H₂ uptake observed during the depth profile.

To demonstrate convincingly that surface-area changes induced by sputtering were an unimportant effect, we performed a second experiment on a Rh surface prepared as above. After characterization of the clean surface by SSIMS, AES, and TDS, it was sputtered (1 KV, 100 nA) and annealed to 525 K. The H₂ TDS peak area increased by no more than 5% compared to the clean surface. This shows that the changes in peak area observed in the depth profile experiment cannot be accounted for by changes in surface area of the Rh.

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