reactions of **6** and **7a** and **7b** were carried out in the presence of acetic anhydride (Ac$_2$O) and triethylamine (NEt$_3$).[10] A solution of **6**, **7a** (1.5 mol equiv), Ac$_2$O (2 mol equiv), and NEt$_3$ (2 mol equiv) in tetrahydrofuran (THF, 30 mmol/mL) was heated under argon at 65 °C (bath temperature) for 10 h, providing the acetylated benzofuran **8** as the only isolated product in a 43% yield (based on **6**).[11] Similarly, heating of **6**, **7b** (1.5 mol equiv), Ac$_2$O (1.1 mol equiv), and NEt$_3$ (1.1 mol equiv) in THF at 65 °C for 72 h under argon produced **9** (28%).[12]

The route to khellin utilizing **8** requires conversion of the acetate to a methyl ether, selective cleavage of the ethyl ether, and pyrone ring formation (Scheme III, eq 1). The first of these objectives was carried out without isolation of the intermediate phenol which, being labile, readily lost the silyloxy group, producing an alkene.[8] Thus, treatment of **8** with sodium hydride (3 mol equiv) and methyl iodide (excess) in HMPA/THF [0 °C then 23 °C] directly produced the methyl ether **10**.[13] The alcohol **11** was freed from its silyl ether [*n*-Bu$_4$NF·3H$_2$O (3 mol equiv), DMF, 23 °C, 85%] and oxidized to the ketone **4** (R = Et) (PDC, CH$_2$Cl$_2$, 53%, 13% recovery of **11**). Selective cleavage of the ethyl ether was effected with BF$_3$·Et$_2$O (10 mol equiv, dry CH$_2$Cl$_2$, 0 °C then 23 °C)[14] to provide **2**.[15,1b–d,f] No demethylated product was detected. Khellin (**1**)[16] was generated from **2** through a Claisen-type condensation and subsequent acid-catalyzed pyrone ring formation.[1c,2]

(8) The reaction of a pyrrole chromium complex **21** with **7a** (THF, 65 °C, 4 h) provided the Diels–Alder dimer **22** (68%) of the expected monomer **23**.
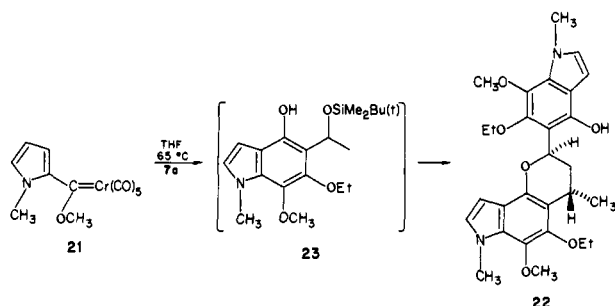
However, under identical conditions, **6** was totally inert to react with **7a**, resulting in the recovery of **6**. Yamashita, A.; Scahill, T. A.; Chidester, C. G. *Tetrahedron Lett.* **1985**, *26*, 1159.

(9) This result was consistent with earlier observations of a dominating steric effect. (a) Dötz, K. H.; Fügen-Köster, B. *Chem. Ber.* **1980**, *113*, 1449. (b) Wulff, W. D.; Tang, P. C.; McCullum, J. S. *J. Am. Chem. Soc.* **1982**, *103*, 7677.

(10) The method was developed with the pyrrole–carbene complex **21** with alkynes. The reaction of **21** with **7a** in the presence of acetic anhydride and triethylamine gave the acetylated product **24** (64%). No Diels–Alder dimer
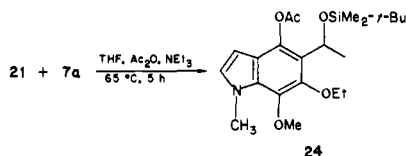
was observed. Yamashita, A.; Scahill, T. A.; Toy, A. *Tetrahedron Lett.* **1985**, *26*, 2969.

(11) All yields refer to isolated yields of analyticaly pure material.

(12) The regiochemistry of two functional groups in **8** and **9** was determined on the basis of the earlier observation; see ref 8. Both reactions of **6** with **7a** and **7b** without triethylamine took considerably longer, and the yields of **8** and **9** were lower. The mechanism and roles of Ac$_2$O and NEt$_3$ in these reactions are presently unestablished.

(13) The reaction presumably proceeded by initial formation of the ketene from the acetate by sodium hydride, followed by methylation of the sodium phenoxide. For example, phenyl acetate was converted to anisole under the same conditions [sodium hydride (2.2 mol equiv), MeI (excess), HMPA, THF, 23 °C].

(14) Methyl ether at the 6-position of the 5-acetyl-4,6,7-trimethoxybenzofuran derivative was selectively cleaved by treatment with AlCl$_3$: Horton, W. J.; Paul, E. G. *J. Org. Chem.* **1959**, *24*, 2000. The mechanism of selective cleavage of ethyl ether in the presence of methyl ethers in the same aromatic ring is presently unestablished.

(15) Mp 97–99 °C; the physical behavior of the product was the same as that of the authentic sample obtained from alkaline degradation of khellin.

(16) Mp 148–150 °C (undepressed on admixture with a natural specimen, mp 151–152.5 °C).

Khellin was also generated from **9** (Scheme III, eq 2). As above, direct conversion of the acetate to the methyl ether was effected by sodium hydride and methyl iodide in THF, providing **12** (68%). Cleavage of the silyl ether (*n*-Bu$_4$NF, DMF, 55 °C) produced an alcohol **13** (89%), which on oxidation (PDC, CH$_2$Cl$_2$) gave the ketone **14** (35%) and the recovered **13** (30%). Oxidation of the *p*-dimethoxy benzene ring of **14** with ceric ammonium nitrate (3 mol equiv) in acetonitrile/water (3:1 mixture) at 0 °C,[17] followed by aqueous acid treatment (1 N HCl, MeOH) led to **3**[18] (70% overall from **14**). The reaction presumably proceeded by CAN oxidation of **14** to a quinone **15**. Under aqueous acid, ketal was cleaved to the β-diketone **5** (R = Et), which with acid cyclized to **3**. Reduction of **3** (NaHSO$_3$, catalytic HCl, 100 °C),[1i] followed by dimethylation (MeI, K$_2$CO$_3$, acetone, reflux), produced **1** (50%) and isokhellin (**16**, 10%).[19]

In summary, we have described two very facile syntheses of khellin in yields of 13% and 5% requiring only six and seven steps, respectively. These results exploit a cycloaddition reaction of a furan chromium carbene complex producing the key intermediates: substituted benzofurans.[20]

Supplementary Material Available: Characterization data (^{1}H NMR, IR, mass and combustion analysis) on all new compounds (4 pages). Ordering information is given on any current masthead page.

(17) Rapoport, H.; Falling, S. N. *J. Org. Chem.* **1980**, *45*, 1260.

(18) Mp 204–208 °C; the physical behavior of the product was the same as that of the authentic sample obtained from oxidation of khellin.

(19) Conversion of Khellinquinone to isokhellin: (a) see ref 1e. (b) Fukushima, S.; Ueno, A.; Akahori, Y. *Chem. Pharm. Bull.* **1964**, *12* (3), 307.

(20) All new compounds isolated during this work have been characterized by satisfactory combustion and spectral (high-resolution mass, IR, NMR) analysis, and these data are recorded as supplementary material.

Photolysis of Dibenzyl Ketones in the Presence of Pentasil Zeolites. Examples of Size/Shape Selectivity and Molecular Diffusional Traffic Control

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The pentasil family of zeolites has received wide attention because of its versatility as catalysts,[1] particularly in size- and shape-selective reactions.[2] The dynamics of molecular diffusion through the differing channel systems of the ZSM-5 have evoked the concept of molecular diffusional traffic control[3] to explain catalytic selectivity in the preparation of *p*-xylene. The latter has been explained in terms of a shape/size effect by which *o*-xylene

(1) For a recent review, see: Minachev, K. M.; Kondralev, D. A. *Russ. Chem. Rev. (Engl. Transl.)* **1983**, *52*, 1113. The pentasil family of zeolites is composed of five-membered rings of (Al,Si)O$_2$ tetrahedra arranged with different crystal symmetries to form zeolites with channels of dimensions of 5–6 Å. The internal surface of LZ-105 is typical of zeolites and the ZSM family, i.e., intersecting channels. For a discussion, see: Derouane, E. G. "Catalysis by Zeolites"; Imelik, B., et al. Eds.; Elsevier: Amsterdam, 1980; p 5.

(2) For recent reviews, see: Csicsery, S. M. *Zeolites* **1984**, *4*, 202. Kokotailo, G. T.; Meier, W. M. *Spec. Publ.—Chem. Soc.* **1979**, *No. 33*, 133.

(3) Derouane, E. G. In "Intercalation Chemistry"; Whittingham, M. S., Jacobson, A. J., Eds.; Academic Press: New York, 1982, p 101. The term "molecular traffic control" was coined to describe selective diffusion within different (linear and zig-zag) channel systems of pentasil zeolites. In the spirit of this concept we extend the term to embrace selective diffusion on the external or internal surface of a pentasil zeolite.

Table I. Relative Yields of Products from Photolysis of o-ACOB and p-ACOB on Pentasil Zeolites. Yields of p-AB or o-AB Normalized to 100%

zeolite	condition[a]	p-ACOB			o-ACOB		
		p-A-p-A	p-AB	BB	o-A-o-A	o-AB	BB
LZ-105	isooctane	0	0	0	270	100	0
	benzene	3	100	3	270	100	220
	benzene (svg)	0	80	3	0	<1	0
Na-ZSM-5	isooctane	0	0	0	65	100	0
	benzene	4	100	3	65	100	55
	benzene (svg)	0	89	0	0	<1	0
Na-ZSM-11	isooctane	0	0	0	25	100	0
	benzene	1	100	1	25	100	25
	benzene (svg)	0	72	0	0	<1	0

[a] Isooctane: After irradiation, the sample was washed with isooctane and then analyzed for products by vapor-phase chromatography (VPC). Benzene: After irradiation, the sample was first washed with isooctane and then with benzene. The two washes were combined and analyzed for products by VPC. Benzene (svg): Samples irradiated in the presence of the radical scavenger TMPO, then washed with benzene, and analyzed for products by VPC. Ratio ketone:TMPO = 1:6.

possesses a shape/size which inhibits its diffusional motion in the ZSM-5 channel system. We have investigated the photochemistry of o-methylbenzyl benzyl ketone (o-ACOB) and p-methylbenzyl benzyl ketone (p-ACOB) sorbed on ZSM-5 and related pentasil zeolites. We report a profound difference in the product distributions of the photolysis of these two ketones on pentasil zeolites depending on the sorption of the ketone and/or photolysis radical fragments into the zeolite framework.[4]

The photochemistry[5] of dry samples o-ACOB and p-ACOB sorbed on the pentasils and related zeolites, LZ-105,[6] Na-ZSM-5,[7] and Na-ZSM-11,[8] was found in the absence of radical scavenger to lead to diarylethanes expected from coupling of benzyl-type radicals resulting from photodecarbonylation of the parent ketone. Mass balances of ~70–80% were achieved in all cases reported in Table I and appear to be limited by the extent of extraction. The product ratios, however, were independent of the extent of extraction. Therefore, we assume the mechanism of photolysis is analogous to that of homogeneous solutions for which random, statistical coupling of radicals occurs. Similar results were observed with photolysis of isooctane slurries of the systems listed in Table I.

The product distributions in the absence of scavenger were determined under two conditions: (a) the products extracted by isooctane and (b) the total products extracted by isooctane and

(4) Zeolite samples were preheated to 500 °C for 1 h immediately before use. Ketones were sorbed onto the zeolites from pentane solution so that ca. 1% ketone (w/w) was adsorbed on the final sample which was prepared by evaporation of the pentane under vacuum (10^{-4} torr). The sample was maintained under vacuum and tumbled during photolysis (313 nm) at ambient temperature.

(5) (a) Turro, N. J.; Kraeutler, B. *Acc. Chem. Res.* **1980**, *13*, 369 and references therein. (b) For other examples of photoreactions of organic molecules adsorbed on zeolites, see: Turro, N. J.; Wan, P. *Tetrahedron Lett.* **1984**, 3655. Turro, N. J.; Wan, P. *J. Am. Chem. Soc.* **1985**, *107*, 678. See also: Suib, S. L.; Kostapapas, A. *Ibid.* **1984**, *106*, 7705. Casal, H. L.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 628.

(6) LZ-105 (Lot 5676-58) was a Linde development sample, Si/Al = 82, pore volume 0.16 cm³/g, crystal density 1.8 g/cm³. Samples were treated with saturated aqueous NaCl solution, dried, and calcined at 500 °C for 1 h. The sample was a generous gift of Dr. E. Flanigen, Union Carbide Technical Center, Tarrytown, NY.

(7) Na,TPA-ZSM-5 (Si/Al = 40) was prepared by the method of Rollman and Volyocsik (Rollman, L. D.; Volyocsik, E. W. *Inorg. Synth.* **1983**, *22*, 61–69) and calcined in flowing air at 60 °C/h to 550 °C, then held at 550 °C for 10 h. The sample was then exchanged 3 times with a 10% NH₄NO₃ solution at 90 °C for 10 h and calcined as described above to give the H form. The material was then exchanged 3 times with a 10% NaNO₃ solution at 90 °C for 1 h, dried, and recalcined as above.

(8) Na,TBA-ZSM-11 (Si/Al = 40) was prepared using a modification of the method of Rollman and Volyocsik (see ref 7). NaAlO₂ (3.6 g) and NaOH (4.8 g) in water (184 g) were added to a second solution containing Ludox (Du Pont) HS-30 silica sol (240 g), tetrabutylammonium bromide (38.68 g), and water (80 g). The resulting gel was stirred under autogeneous pressure at 160 °C for 24 h, and the solid produced was thoroughly washed and dried at 110 °C. The X-ray powder diffraction pattern corresponded to that of Na,TBA-ZSM-11 as described by Argauer and Landolt (U.S. Patent 3 702 886, 1972) and Chu (U.S. Patent 3 709 997, 1973). The zeolite was calcined in flowing air at 60 °C/h to 550 °C, then held at 550 °C for 10 h. The sample was then exchanged above to produce the H form. This material was then exchanged 3 times with a 10% NaNO₃ solution at 90 °C for 1 h, dried, and recalcined as above.

Table II. o-Xylene Sorption Results for Pentasil Zeolites[a]

zeolite	wt % of o-xylene sorbed time of exposure, h			
	2	5	22	45
LZ-105	0.75	0.75	0.88	1.14
Na-ZSM-5	0.74	0.93	1.40	2.00
Na-ZSM-11	4.36	5.12	6.78	8.06

[a] Each zeolite sample was placed in a cell containing a vacuum stopcock and outgassed at 425 °C in vacuum to remove volatiles and obtain a dry weight. The zeolites were then exposed to ~1.7 mm of o-xylene vapor at room temperature using an apparatus similar to that described by: Landolt, G. R. *Anal. Chem.* **1971**, *43* 613. o-Xylene was chosen because its sorption into the zeolite frameworks (vs. surface) mimics the sorption of o-AB and the o-A photolysis fragments. Weight gains were recorded for various exposure times; the amount on the external surface could then be estimated by extrapolation to $t = 0$. The amount in the framework would then be the total amount sorbed at any time minus the amount on the external surface. Additional experiments, not reported here, correspond to such sorption exposure measurements.

benzene via sequential extractions. Isooctane is expected, because of its size,[9] to extract products from the external surface of the zeolite, whereas benzene is able to extract products from the internal surface of the zeolite framework.

The presence of an efficient free radical scavenger (2,2,6,6-tetramethylpiperidin-1-oxyl, TMPO)[10] during the photolysis of o-ACOB prevented the formation of o-A-o-A, o-AB, and BB as products (Table I). Therefore, the radicals produced during the photolysis were completely accessible to the TMPO molecule, *indicating that the o-ACOB was sorbed only on the exterior surface of the zeolite.* Carbonyl-containing structures were observed among the scavenging products which suggests that duffusion on the external surface is relatively rapid, since the rate of decarbonylation of $ArCH_2CO$ radicals is of the order of 10^8 s^{-1} in solution at ambient temperature.[11]

Photolysis of p-ACOB in the presence of TMPO, however, resulted in the formation of p-AB only, *indicating the p-ACOB was sorbed in the zeolite framework during photolysis.* In the absence of a radical scavenger, photolysis of p-ACOB produced small amounts of p-A-p-A and BB compared to p-AB, consistent with a significant fraction of geminate pair recombination for each system. The photolysis product distributions, with and without the presence of TMPO, are virtually identical for the several pentasil samples, again consistent with the conclusion that p-ACOB is sorbed into their frameworks.[12]

(9) Isooctane is too large to be sorbed rapidly into the pentasil structures: Jacobs, P. A.; Martens, J. A.; Weikamp, J.; Beyer, H. K. *Faraday Discuss. Chem. Soc.* **1981**, *No. 72*, 353.

(10) For the use of this stable free radical to scavenge the fragments of ketone homolysis, see: Hageman, H. J. *Makromol. Chem.* **1984**, *185*, 1795.

(11) Turro, N. J.; Gould, I. R.; Baretz, B. H. *J. Phys. Chem.* **1983**, *87*, 531. The rate of decarbonylation, of course, may be somewhat different on solid surfaces. The implied fast rate of sieving may result from partial inclusion of the B portion of o-ACOB in the apertures on the external surface of LZ-105.

In contrast, the product distribution for the photolysis of *o*-ACOB depends on the zeolite substrate (Table I). As shown in Table II, sorption of *o*-xylene from the vapor phase highlights the differences in the zeolites. The sorption rate of *o*-xylene into LZ-105 is so small that it must be concluded that virtually all of the *o*-ACOB for this sample is sorbed on the exterior. This conclusion is consistent with the observation that isooctane extraction is able to completely recover the oAoA and oAB photolysis products. That the oA segment is too large to enter the framework channels is consistent with the *o*-xylene sorption results. The absence of BB product in the isooctane wash indicates that it resides within the zeolite framework. We postulate that the molecule *o*-ACOB may be sorbed on the zeolite surface in two orientations, one where the entire ketone molecule is on the outer surface and another where the smaller segment of the ketone intrudes into the channel opening, whereas the larger segment of the ketone must remain on the outer surface.

From Tables I and II we conclude that no *o*-AB is formed within the zeolite framework for LZ-105. The difference between the observed product distributions and those of a solvent random radical coupling can be attributed to rapid B· radical sieving. The sieved B· radicals are inhibited from coupling with *o*-A· radicals which must remain on the external surface. As a result, *o*-A-*o*-A and BB coupling becomes dominant over *o*-AB coupling.[13]

For ZSM-5, because the product distribution is the same as that for random radical couplings, we propose that BB coupling occurs predominately on the external surface, and that BB molecules are sieved into the internal surface after they are formed. For ZSM-11, although the BB coupling/sorption mechanism seems to be operating, there is an excess of *o*-AB formed, because some *o*-ACOB was absorbed prior to photolysis. From the xylene sorption data, the ratio of surface to framework photolysis is expected to strongly depend on the sorption exposure time (Table II) and temperature. Indeed, longer times and higher temperature favor more *o*-ACOB entering the framework resulting in a greater cage effect and *o*-AB, therefore, becomes the major product.[14]

In summary, the photolyses of *o*-ACOB in the presence of pentasil zeolites follow strikingly different pathways due to the shape selectivity and molecular diffusional (traffic control)[3] characteristics of radicals on the zeolite surfaces. The *p*-ACOB is adsorbed on the internal surface, because the *p*-A moiety has access to the zeolite internal structure. Depending on the sorption into the framework, photolysis product distributions of *o*-ACOB can be dramatically varied. The different photochemical results are the consequence of the diffusional and chemical dynamics available to the radicals produced by homolytic photochemical cleavage of the ketone. The sieving of radicals relative to surface reaction depends on relative diffusional processes that will be sensitive to zeolite structure and factors such as extent of dehydration. We are currently investigating these aspects of molecular diffusion traffic control of radicals adsorbed on zeolites.

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(12) The small amount of *p*-A-*p*-A and BB observed may be produced by recombination of *p*-A and B radicals on the zeolite surface, from recombination within the framework of radicals generated within the framework, or from recombination on the surface of radicals generated within the framework following their migration to the surface. The inability of isooctane to extract products lends further evidence to their generation within the zeolite framework.

(13) The *o*-AB formed on the exterior must be accompanied by *o*-A-*o*-A 100 parts oAB correspnds to 50 parts each of *o*-A-*o*-A and BB. As such, approximately 67% of the product distribution for LZ-105 is the result of B· radical sieving.

(14) For the example given in Table I, assuming the *o*-A-*o*-A observed is from the surface photolysis, the internal contribution to the product distribution is approximately 33%.

Triplet Energy Transfer as a Probe of Surface Diffusion Rates: A Time-Resolved Diffuse Reflectance Transient Absorption Spectroscopy Study

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The importance of molecular diffusion to surface photochemistry has been well established.[1] However, no direct measurements of surface diffusion rates have been reported nor have any correlations been established between molecular structure and rates of diffusion. Extraction of diffusion rate constants from fluorescence quenching experiments is complicated by contributions from resonant energy transfer.[2] Triplet energy transfer proceeds via an exchange mechanism, which requires direct overlap of donor and acceptor orbitals.[3] In homogeneous solution, exothermic transfer occurs at diffusion-controlled rates.[3] The rate constant of triplet energy transfer between surface adsorbed molecules should provide a lower bound for surface diffusion. We report the first time-resolved measurements of triplet energy transfer on silica surfaces, employing time-resolved diffuse reflectance transient absorption spectroscopy.[4]

Irradiation (Excimer laser, 351 nm, 20-ns fwhm, <10 mJ) of benzophenone (BZP 10^{-5}–10^{-4} mol/g of silica) adsorbed on 22, 95, or 255 Å silicas[5] yield transient absorption spectra with maxima at 520 nm[6] (Figure 1). The transient decay on 255 Å silica is exponential with a lifetime of 1.2 μs and is quenched by O_2 and butadiene with rate constants of $(4.5 \pm 0.1) \times 10^4$ and $(5.0 \pm 0.2) \times 10^7$ torr^{-1} s^{-1}. On 22 and 95 Å silicas, the decays are nonexponential with first half-lives of 1–2 and 3–5 μs. We assign this transient to the triplet state of benzophenone, ^{3}BZP*, by comparison with previous homogeneous solution[7] and surface studies.[4a]

The transient spectra and decays resulting from irradiation of coadsorbed BZP and naphthalene, NP, are very different. The initial transient signal size observed at 520 nm (410 nm) decreases (increases) with increasing NP loading. The transient decays at 520 nm, on 95 and 255 Å silicas, are exponential for NP loadings ≥6 and 2 μmol/g, respectively; the decay rate constants increase with NP loading (Figure 2). At the lowest NP loading, the decay half-life at 410 nm is 30 μs.[8] The transient absorption spectrum observed, after ^{3}BZP* decays exhibits a maximum at 410 nm

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(3) (a) Sandros, K.; Backstrom, H. L. J. *Acta Chem. Scand.* **1962**, *16*, 958. (b) Wilkinson, F. *Adv. Photochem.* **1964**, *3*, 241. (c) Ternin, A. N.; Ermolaev, V. L. *Trans. Faraday Soc.* **1956**, *52*, 1042. (d) Smaller, B.; Avery, E. C.; Remko, J. R. *J. Chem. Phys.* **1965**, *43*, 922.

(4) (a) Wilkinson, F.; Willsher, C. J. *Chem. Phys. Lett.* **1984**, *104*, 272. (b) Kessler, R. W.; Krablicher, W.; Uhl, S.; Oelkrug, D.; Hagan, W. P.; Hyslop, J.; Wilkinson, F. *Opt. Acta* **1983**, *30*, 1099.

(5) 22, 95, and 255 Å silicas have surface areas of 888, 571, and 78 m²/g.[14a,b] The number is the average pore diameter in angstroms. The first two silicas are fibrous. The latter is aggregated. Samples were made by adsorption from pentane followed by slow solvent evaporation and evacuation to 1 mtorr.

(6) Signals are analyzed as $\Delta R/R$; R is the reflected light intensity.[4] Decays are quoted as exponential when log ($\Delta R/\Delta R_0$) vs. t is linear for >3 half-lives.

(7) (a) Topp, M. R. *Chem. Phys. Lett.* **1975**, *32*, 144. (b) Beckett, A.; Porter, G. *Trans. Faraday Soc.* **1963**, *59*, 2038.

(8) Irradiation of NP adsorbed without BZP produces no transients.