

a 1269-cm⁻¹ a_g fundamental. We would point out here that, unless the 627-cm⁻¹ mode has a large positive anharmonicity (which seems unlikely), at least one of the Fermi split bands would be lower in frequency than $2 \times 627 = 1254$ cm⁻¹. However, there are many other a_g overtones and combination levels of approximately the correct energy to enter into Fermi mixing with the a_g fundamental whose zero-order energy is near 1260 cm⁻¹.

Of the remaining unassigned weak bands, the one at 1185 cm⁻¹ is assigned as b_{1g} as indicated by the Raman data.¹⁷ Three other bands at 1233, 1348, and 1523 cm⁻¹ are consistently observed in all three Shpol'skii solvents, but the frequencies do not fit well with either an a_g combination band or b_{1g} vibronically induced fundamental interpretation. Given the uncertainty in the preceding analysis, there is little point in further speculating about these minor features at this time.

Summary and Conclusions

The influence of chemical substitution on fluorescence vibronic patterns has been systematically studied in nine simply substituted anthracenes. All nine totally symmetric fundamental vibrational frequencies of anthracene (exclusive of C-H stretches) have been assigned, and the results are in agreement with Raman data.¹⁷ Symmetry breaking by the chemical substitution has been shown to

have only a small effect on the number of fluorescence active vibrations. The evidence for S_1 - S_3 vibronic coupling and S_0 Fermi resonance in the parent compound has been discussed, although further work will be required for a more definitive analysis.

We are currently performing Franck-Condon factor calculations using the experimental fluorescence intensities to determine S_1 equilibrium geometries. If the intensity of the carbon-halogen stretches in 9,10-DCA and 9,10-DBA is assumed to depend only on the carbon-halogen bond length change upon electronic excitation, a bond length change of 0.003 nm is inferred. Preliminary studies of the fluorescence spectra of amino- and nitroanthracenes are in progress. These substituents, and others such as CN, OH, and OCH₃, are of interest because they can be expected to exert more substantial perturbations on the electronic and vibronic structure.

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Reaction of Tetrathiafulvalene with Haloalkanes

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A kinetic study of the photochemical reaction of TTF with haloalkanes has been made. The results are largely in agreement with a mechanism suggested by Scott and co-workers, but some additional findings of fundamental importance were obtained. An improved photosynthesis of TTFCl_{0.68} is reported.

Introduction

A strong interest has been shown in the cation radical complexes formed by tetrathiafulvalene (TTF) with halogen acceptors,¹ especially since these salts have high electron conductivity in the crystalline state.² Scott and co-workers³ discovered that TTF and several of its derivatives undergo photooxidation in solutions containing halocarbons, producing mixed-valence salts, TTFX_y, where y lies in a narrow range, e.g., 0.68 ± 0.03 for $X = Cl$. Later,⁴ it was found that this photochemical procedure was the best for preparing TTFCl_{0.68}.

The IBM group suggested³ that the mechanism of that photooxidation involved excitation of the charge-transfer

(CT) complex expected to form between TTF and a haloalkane such as CCl₄, followed by decomposition of the complex into the radical cation which would then combine with excess TTF to form the mixed-valence salt.

Their evidence for that mechanism was limited to the behavior of the CT absorption band at different concentrations of CCl₄ as acceptor. As they pointed out, detailed kinetic study would be required to establish the process. They proposed the mechanism in analogy to the mechanism proposed earlier for photochemical CT reactions in halocarbon solutions for ferrocene^{5,6} and, in this laboratory, for alkylamines.⁷

We have made a kinetic study of the photooxidation of TTF in solutions of CCl₄, CHCl₃, and C₂Cl₆. The results are shown to be largely in accord with the prediction of Scott and co-workers³ but with some additional findings of fundamental importance. Our work has also led to an

(1) Wudl, F.; Smith, G. M.; Hufnagel, E. J. *J. Chem. Commun.* 1970, 1453-4.

(2) Wudl, F.; Wobschall, D.; Hufnagel, E. J. *J. Am. Chem. Soc.* 1972, 94, 670-2.

(3) Scott, B. A.; Kaufman, F. B.; Engler, E. M. *J. Am. Chem. Soc.* 1976, 98, 4342-4.

(4) Scott, B. A.; LaPlaca, S. J.; Torrance, J. B.; Silverman, B. D.; Welber, B. *J. Am. Chem. Soc.* 1977, 99, 6631-9.

(5) Brand, J. C. D.; Sneddon, W. *Trans. Faraday Soc.* 1957, 53, 894-900.

(6) Traverso, O.; Scandola, F. *Inorg. Chim. Acta* 1970, 4, 493-8.

(7) Biaselle, C. J.; Miller, J. G. *J. Am. Chem. Soc.* 1974, 96, 3813-6.

improved synthesis of $\text{TTFCl}_{0.68}$.

Experimental Section

Materials. Aluminum oxide (neutral, Camag), ethanol (200 proof, Pharmco), hexachloroethane (reagent grade, MC/B), 1,10-phenanthroline monohydrate (reagent grade, G. Frederick Smith Chemical Co), potassium oxalate (analytical reagent, Baker, and 1,1,2,2-tetrachloroethane (reagent grade, Aldrich) were used as received.

Argon (Airco) and nitrogen (prepurified, Airco) were passed over Drierite before use. Carbon tetrachloride and chloroform (both spectroquality, MC/B) were stored over Linde, Type 4A molecular sieves.

Ligroin (purified, Eastman) was shaken three times with 10% by volume of concentrated H_2SO_4 .⁸ The lower stratum of acid was drawn off and the ligroin was then shaken twice with H_2O , once with 10% Na_2CO_3 , and once again with water. It was next dried over MgSO_4 and distilled, the material of boiling range 58–64 °C being collected. Finally, it was passed through a 25-cm column of Al_2O_3 and it was deoxygenated before use by bubbling argon through it for 15 min.⁹

TTF (reagent grade, Aldrich) was used without further purification for synthetic runs. For kinetic runs it was purified by recrystallization three times from ligroin under argon.⁹ It was wrapped in filter paper and put in a small beaker which was placed inside a bomb containing some Drierite. The bomb and contents were purged with argon for 5 min, then filled with argon and stored in a desiccator in a refrigerator.

Preparation of Samples and Kinetic Measurements. The reagents were purged with nitrogen for at least 15 min before use. The solutions were prepared in the dark. Ultraviolet and visible absorption spectra were recorded with a Cary Model 14 spectrophotometer the stoppered cells of which were thermostated by water circulated from a Wilkens-Anderson Lo-Temp bath. The cell holder was placed in a black container which was purged continuously with nitrogen. Silica cells of 1.0 cm thickness and the percent-transmittance slidewire of the spectrophotometer were employed.

The solutions were irradiated with a U.V. Products Model UVL-21 long-wave ($\lambda = 366\text{nm}$) lamp. The solutions were stirred magnetically with a Thomas No. 8608-E62 stirring button.

All of the reactions were run at 25 °C. They were followed spectroscopically by studying the product and reactant peaks. The halocarbon was always in large excess and ethanol was used as solvent throughout because $\text{TTFCl}_{0.68}$ is insoluble in halocarbons. Before starting the reaction, neat ethanol was placed in both the sample and the reference cells and the UV-visible spectrum was taken. At zero time (not irradiated), the solution to be irradiated was placed in the sample cell and the spectrum was recorded. Then the solution in the sample cell was irradiated with the 366-nm UV lamp for a recorded time and the spectrum was recorded again.

Actinometry and Quantum Yields. The potassium ferrioxalate system developed by Hatchard and Parker¹⁰ and modified by Baxendale and Bridge¹¹ was used in the actinometry. The measurements of the quantum yields

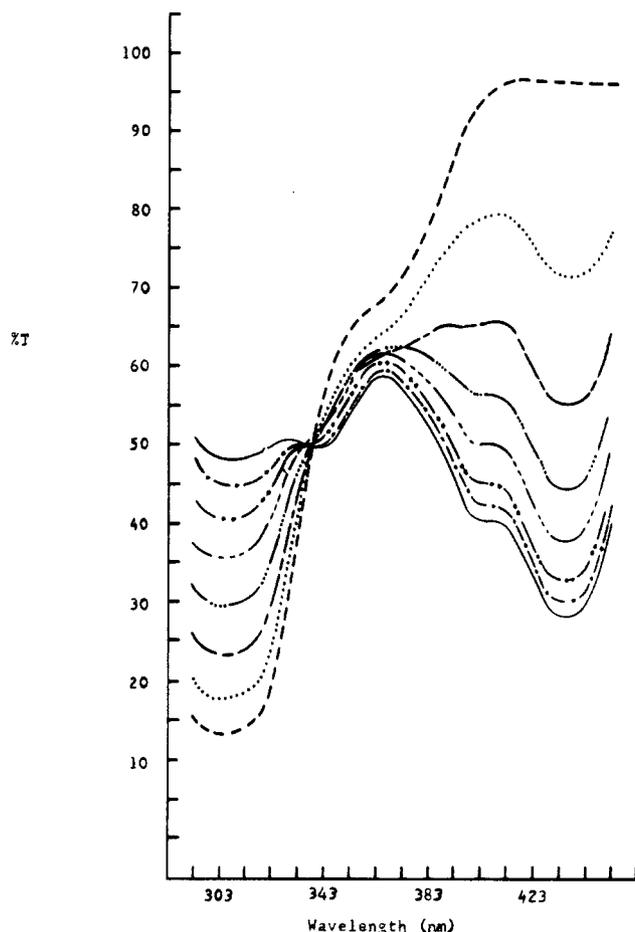


Figure 1. Kinetic run for reaction of TTF with CCl_4 . $[\text{TTF}] = 7.8 \times 10^{-5} \text{ M}$, $[\text{CCl}_4] = 2.47 \text{ M}$. Time (min): (----) 0; (....) 5; (- · - ·) 10; (- - - -) 15; (- - - -) 20; (- · · ·) 25; (- · · ·) 30; (—) 35.

TABLE I: First-Order Rate Constants for the Reaction of TTF with CCl_4 in Ethanol at 25 °C

$10^4[\text{TTF}], \text{M}$	0.78	0.78	0.78	1.55	2.33	2.34	2.34
$[\text{CCl}_4], \text{M}$	1.24	2.47	3.71	2.47	2.47	2.47	2.47
$10^4 k, \text{s}^{-1}$	3.17	4.95	5.39	4.17	3.54	3.30	3.28

TABLE II: Quantum Yields (Φ) of Product at Different Initial Concentrations of Reactants

haloalkane	10^4 [TTF], M	[haloalkane], M	Φ
CCl_4	0.78	2.47	0.98
	1.55	2.47	0.85
	2.33	2.47	0.99
	0.78	3.71	1.07
	0.78	1.24	0.52
	2.34	2.47	0.66
	2.34	2.47	0.66
CHCl_3	1.56	10.45	0.14
	1.56	6.97	0.16
	0.78	10.45	0.14
C_2Cl_6	1.56	0.285	0.15
	1.56	0.190	0.10
	0.78	0.190	0.09

of the product were carried out with the 366-nm lamp and at 25 °C.¹² Those measurements were carried to conversions as high as 60% and were extrapolated back to the Φ value at the start of reaction in each case.

(12) For details see the Ph.D. Dissertation of B. Vessal, University of Pennsylvania, 1979. The values of Φ given in the dissertation are too high by a factor of 400.

(8) Vogel, A. I. "A Textbook of Quantitative Inorganic Analysis"; Wiley: New York, 1961; 3rd ed.

(9) Gemmer, R. V.; Cowan, D. O.; Poehler, T. O.; Bloch, A. N.; Pyle, R. E.; Banks, R. H. *J. Org. Chem.* **1975**, *40*, 3544–7.

(10) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. (London)*, *Ser. A* **1956**, *A235*, 518–36.

(11) Baxendale, J. H.; Bridge, N. K. *J. Phys. Chem.* **1955**, *59*, 783–8.

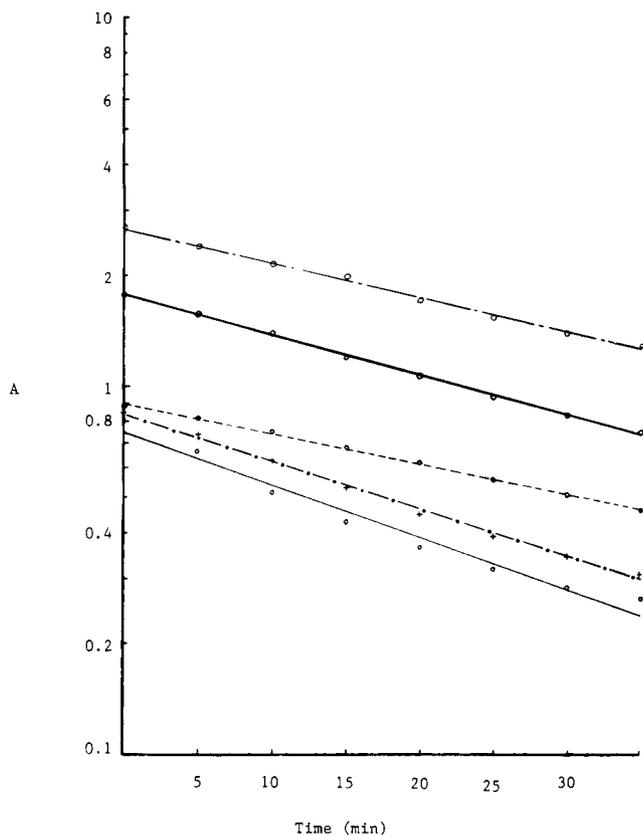


Figure 2. First-order rate plots for TTF- CCl_4 mixtures: (—) $[\text{TTF}] \times 10^4$, $M = 0.78$, $[\text{CCl}_4]$, $M = 3.71$; (- · -) 0.78, 2.47; (- - -) 0.78, 1.24; (—) 1.55, 2.47; (- - -) 2.33, 2.47.

Results

Kinetic Studies. The CT band at 335 nm is difficult to study due to its proximity to the intense bands of TTF at 303 and 316 nm and to the product band at 340 nm. For that reason, we followed the disappearance of the TTF band at 303 nm and the formation of the product band at 436 nm. Figure 1 shows the changes in those bands in a typical run. The isosbestic point shows that the absorption is due nearly entirely to reactant and product. When $\ln A$ of the TTF peak at 303 nm was plotted against time of irradiation, a linear plot resulted for all of the halocarbons studied (see, for example, Figure 2). The first-order rate constants were calculated from the slope and are listed in Table I for the TTF- CCl_4 reaction. When the halocarbon was chloroform, the average value of k was $1.1 \times 10^{-4} \text{ s}^{-1}$ and with hexachloroethane it was $5.0 \times 10^{-5} \text{ s}^{-1}$. The quantum yields are given in Table II.

Syntheses of $\text{TTFCl}_{0.68}$ and $\text{TTFCl}_{0.77}$. The only method published for the synthesis of $\text{TTFCl}_{0.68}$ up to the present has been that discovered by Scott and co-workers.^{3,4} They irradiated a solution of 2 mmol of TTF in 100 mL of CCl_4 with a 365-nm UV lamp (0.5 mW/cm^2) for 3 h, obtaining 135 mg of crude product (29.5% yield).

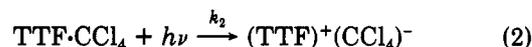
The following improved synthesis was discovered here. A solution of 2 mmol of TTF in 50 mL of CCl_4 was irradiated with a 254-nm UV lamp (3.0 mW/cm^2 at 1 in.). After 1 h of radiation, 403 mg (88.1% yield) of crude product was collected and was recrystallized from hot ethanol, yielding 126 mg of pure product (27.5% yield). Anal. Calcd for $\text{C}_6\text{H}_4\text{S}_4\text{Cl}_{0.68}$: C, 31.55; H, 1.76; S, 56.13; Cl, 10.55. Found (Galbraith Labs.): C, 31.40; H, 1.82; S, 56.10; Cl, 10.74.

We were surprised to find that TTF reacted rapidly with $\text{CHCl}_2\text{CHCl}_2$ in the dark. We also discovered that the product was $\text{TTFCl}_{0.77}$ which is formed in the dark reaction

of TTF with chlorine.⁴ Analysis of the $\text{CHCl}_2\text{CHCl}_2$ revealed that it contained chlorine as an impurity. Further study showed that this provides a convenient synthesis of $\text{TTFCl}_{0.77}$ without use of a large amount of chlorine.

Discussion

Our work indicates that the mechanism suggested by Scott and co-workers³ may be rewritten as follows:



For step (1), with CCl_4 in excess, as in our case, we have

$$K = k_1/k_{-1} = \frac{[\text{TTF} \cdot \text{CCl}_4]}{([\text{TTF}] - [\text{TTF} \cdot \text{CCl}_4])[\text{CCl}_4]} \quad (6)$$

Rearranging (6) yields

$$[\text{TTF} \cdot \text{CCl}_4] = K[\text{TTF}][\text{CCl}_4]/(1 + K[\text{CCl}_4]) \quad (7)$$

Assuming steady-state concentrations for the radical, $\cdot\text{CCl}_3$, the exciplex, $(\text{TTF})^+(\text{CCl}_4)^-$, and the intimate ion pair, TTF^+Cl^- , we obtain the equations:

$$k_4[\text{TTF}^+\text{Cl}^-]^x[\text{TTF}]^{(1-x)} = k_2I[\text{TTF} \cdot \text{CCl}_4] = k_3[\cdot\text{CCl}_3]^2 \quad (8)$$

The rate of disappearance of TTF is then as follows:

$$-d[\text{TTF}]/dt = k_1[\text{TTF}][\text{CCl}_4] - k_{-1}[\text{TTF} \cdot \text{CCl}_4] + k_4[\text{TTF}^+\text{Cl}^-]^x[\text{TTF}]^{(1-x)} \quad (9)$$

Substituting for $[\text{TTF}^+\text{Cl}^-]^x[\text{TTF}]^{(1-x)}$ and $[\text{TTF} \cdot \text{CCl}_4]$ from (8) and (7) yields the following rate equation:

$$-d[\text{TTF}]/dt = \frac{\{K(k_1[\text{CCl}_4] + k_2I)/(1 + K[\text{CCl}_4])\}[\text{TTF}][\text{CCl}_4]}{\quad} \quad (10)$$

Since CCl_4 is in large excess, (10) can be written as

$$-d[\text{TTF}]/dt = k[\text{TTF}]$$

which is in agreement with the experimental data (see Figure 2 and Table I).

Equation 10 predicts that the relative rates for different halocarbons will be determined by the relative values of k_1 and k_2 all else being the same. In turn, one should expect that those constants would be proportional to the electron affinities of the halocarbons. As this predicts, CCl_4 , which has a higher electron affinity¹³ than CHCl_3 and a higher wavelength for its CT band maximum (335 nm compared with 330 nm), does have a greater velocity constant.

As stated earlier, the isosbestic point shown in Figure 1 portrays a lack of large concentrations of intermediates, which agrees with the mechanism. The quantum yields show that the free radicals do not produce chain reactions. The C_2Cl_6 product of the termination step causes no difficulty by reacting with the TTF since it is never present in appreciable amount.

Step (4) is not to be written as an equilibrium step. When TTF is added to solutions of $\text{TTFCl}_{0.68}$ in ethanol

the composition of the chloride does not change. Earlier, Scott and colleagues³ suggested that "use of solvents in which the mixed valence phases have greater solubilities should allow the direct photochemical preparation of compounds having higher TTF^+/TTF^0 ratios". It is also interesting that $TTFCl_{0.68}$ does not dissociate in solution as shown by the fact that the UV spectrum of $TTFBr_{0.71}$

is different from that of $TTFCl_{0.68}$. In ethanol solution the principal bands for $TTFCl_{0.68}$ are at 340, 436, and 575 nm while those for $TTFBr_{0.71}$ are at 345, 447, and 605 nm.

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Oxygen-18 Exchange between Zeolite ZSM-5 and Water

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Porotectosilicate frameworks of zeolites, including high silica materials, are considerably more reactive than we tend to think. This has been demonstrated by studies of ^{18}O exchange between high-purity samples of synthetic zeolite ZSM-5 in the ammonium form and liquid water at 95 °C. The investigation of the ^{18}O -exchange kinetics revealed a two-step reaction which can be interpreted in terms of hydroxyl groups exchanging relatively rapidly (primary exchange) and oxygen atoms from T-O-T bridges exchanging at a rate about 40 times slower (secondary exchange). Since the T sites in ZSM-5 contain mostly Si and only minor amounts of Al, the reported findings imply that not only Si-O-Al but also Si-O-Si bridges are cleaved under relatively mild conditions in the presence of water.

Introduction

The work reported here was to provide information on oxygen exchange between water and the important high silica zeolite ZSM-5, including its Al-free end member.

By combining ^{18}O exchange with IR,¹ thermal gravimetric analysis (TGA), and temperature-programmed desorption (TPD) of ammonia, the number of hydroxyl groups from Brønsted acid sites and from terminal silanol groups could be determined quantitatively. The primary exchange capacity of gel and low-crystallinity materials has been noted to exceed greatly that of pure zeolite samples.¹⁵ Thus, exchange reactions with ^{18}O enriched water are also a sensitive means for detecting small amounts of these common impurities in samples of synthetic zeolites.

The surfaces of a number of oxide catalysts have been studied by $^{18}O_2$ exchange at elevated temperatures,² but no exchange between $^{18}O_2$ and zeolites X, Y, and mordenite was observed below 600 °C.³ Adsorbed $C^{18}O_2$ was reported to exchange ^{18}O only on heating the samples to temperatures of 200–500 °C.⁴ The rate of exchange at 300 °C could be correlated with the C_7 -cracking activity of the zeolite. More recently, extensive ^{18}O exchange was reported to occur at 200–300 °C between $C^{18}O_2$ and zeolite X, while zeolite Y was found to exchange considerably less.⁵ No Si-O-Si bonds were cleaved in these reactions since the exchange mechanism involved the formation of a surface carbonate species associated with the charge-balancing Na^+ cations of the AlO_4^- tetrahedra.

Exchange reactions between $H_2^{18}O$ and silica glass,⁶ feldspars,⁷ and X-ray amorphous catalyst materials⁸ have

been studied before. Silica glass and feldspars were found to exchange ^{18}O in the temperature range 360–1100 °C and pressures of up to 600 bars. The mobility of framework atoms in feldspars was thus demonstrated.⁷ Amorphous aluminosilicate cracking catalysts were observed to exchange ^{18}O in two steps at 450 °C.⁸ The first was attributed to exchange of hydroxyl oxygen, and the second (slower) step to exchange of oxygen from T-O-T (T = Si, Al) bridges.

ZSM-5 with Si/Al ratios ranging from ~10 to >4000⁹ has been synthesized from highly siliceous systems containing tetrapropylammonium (TPA) and sodium ions.¹⁰ The crystal structure and the structure-related properties of the porosilicate framework of ZSM-5 have been described previously.^{11–14}

Experimental Section

High-purity ZSM-5 samples were crystallized from dilute systems containing around 15–20 mg of solid per cm^3 of solution.¹⁵ Typical molar compositions of the synthesis mixtures were as follows: 21–36 $SiO_2:Al(NO_3)_3:8.5–10.5 NaOH:57–72 TPA(OH):10–11 NH_4OH:2600–3300 H_2O:425–533 C_3H_5(OH)_3$. Crystallizations were carried out at 200 °C for 5–6 days in 1-L autoclaves equipped with

(7) Wyart, J.; Sabatier, G.; Curien, H.; Ducheylard, G.; Séverin, M. *Bull. Soc. Fr. Minéral. Cristallogr.* **1959**, *82*, 387.

(8) Oblad, A. G.; Hindin, S. G.; Mills, G. A. *J. Am. Chem. Soc.* **1953**, *75*, 4096.

(9) Olson, D. H.; Haag, W. O.; Lago, R. M. *J. Catal.* **1980**, *61*, 390.

(10) Argauer, R. J.; Landolt, G. R. U.S. Patent 3702886, 1972.

(11) Kokotailo, G. T.; Lawton, S. L.; Olson, D. H.; Meier, W. M. *Nature (London)* **1978**, *272*, 437.

(12) Kokotailo, G. T.; Meier, W. M. *Chem. Soc. Spec. Publ.* **1980**, *33*, 133.

(13) Olson, D. H.; Kokotailo, G. T.; Lawton, S. L.; Meier, W. M. *J. Phys. Chem.* **1981**, *85*, 2238.

(14) Wu, E. L.; Lawton, S. L.; Olson, D. H.; Rohrman, A. C.; Kokotailo, G. T. *J. Phys. Chem.* **1979**, *83*, 2777.

(15) von Ballmoos, R. Ph.D. Thesis, ETH, Zurich, 1981. "The ^{18}O -Exchange Method in Zeolite Chemistry: Synthesis, Characterization and Dealumination of High Silica Zeolites", in "Texte zur Chemie und Chemietechnik"; Salle & Sauerländer: Frankfurt, 1981.

(1) Jacobs, P. A.; von Ballmoos, R. *J. Phys. Chem.* In press.

(2) Novakova, J. *Cat. Rev.* **1970**, *4*, 77.

(3) Antoshin, G. V.; Minachev, Kh. M.; Sevastjanov, E. N.; Kondratjev, D. A.; Newy, C. Z. *Adv. Chem. Ser.* **1971**, *No. 101*, 514.

(4) Peri, J. B. *J. Phys. Chem.* **1975**, *79*, 1582.

(5) Gensse, C.; Anderson, T. F.; Fripiat, J. J. *J. Phys. Chem.* **1980**, *84*, 3562.

(6) Roberts, J. P.; Moulson, A. *J. Nature (London)* **1958**, *182*, 200.