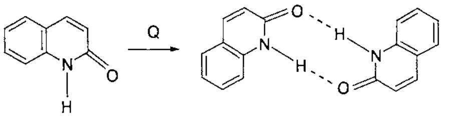
Spectroscopic and Photophysical Behavior of 2-Quinolone as a Probe for Brønsted and Lewis Acid Sites in Zeolites

Masanobu Kojima,* Akira Odaka,† Tsuyoshi Nakajima,*† and Yasunao Kuriyama††
Department of Bioscience and Biotechnology, Faculty of Agriculture, Shinshu University, Asahi, Matsumoto, Nagano 390-8621
†*Department of Chemistry and Material Engineering, Faculty of Engineering, Wakasato, Nagano 380-8553*
††*Department of Chemistry, School of Science, Kitasato University, Sagamihara, Kanagawa 228-8555*

(Received April 2, 1999; CL-990246)

Brønsted and Lewis acid sites in zeolites were characterized by using 2-quinolone as a probe, by means of ultraviolet and infrared absorption spectra, fluorescence decay lifetime, and ESR. The results showed clearer differences in the acidity of zeolites compared to those determined by using Hammett indicators. The species observed in the zeolites depended on the acidity, the cavity size, and the amount of 2-quinolone loaded.

In order to make further advances on recent studies of intrazeolite photochemistry,[1] it is essential to evaluate the effects of Brønsted and Lewis acid sites in the zeolite cavities on the photophysical and photochemical behavior of organic guest molecules.[2-6] The spectroscopic properties of the ground and excited states of 2-quinolone (Q) in solution have been investigated in the absence and presence of proton[7] and the strong Lewis acid BF_3.[8] In particular, it is interesting that in nonaqueous solution[9] and in the solid state[10] Q exists in the form of the hydrogen-bonded dimer (Eq. 1). Therefore, it seems probable that comparison of the spectroscopic behavior of Q in solution with that in zeolite can be used to determine the acidity of the sites existing in the cavities and the effect of the acid sites on complexation. We have studied the spectroscopic behavior of Q in zeolites and on silica gels by means of ultraviolet (UV) and infrared (IR) absorption spectra, fluorescence decay lifetime,[11] and ESR. On the basis of the results we report here that the interaction of Q with the acid sites and the dimer formation in zeolites can be correlated to the acidity, the cavity size, and the amount of Q loaded.



Q

(1)

The effect of the Brønsted acid HCl in CH_2Cl_2 on the ground and excited states of Q was determined by the measurement of UV absorption spectra and fluorescence decay lifetime (τ/ns) as studied for the Q-BF_3 complex.[7,8] Addition of the 0.5, 1, and 2 equiv. of HCl-OEt_2 into the CH_2Cl_2 solution including Q (10^{-4}M) caused significant change in the absorption spectra as shown in Figure 1. It is likely that the red shift of the absorption band around 230-nm wavelength and the blue shift of the long-wavelength absorption band occurred due to complexation with the carbonyl group as in the case of Q-BF_3 complex.

As can be seen in Table 1, the lifetimes of Q (10^{-4} M) depended on the solvent. In CH_2Cl_2, only one component with a lifetime of 0.16 ns was observed, in close agreement with the

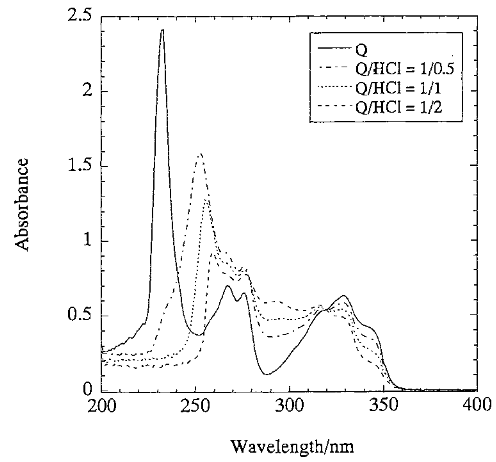


Figure 1. UV absorption spectrum of 2-quinolone (1×10^{-4} M) in CH_2Cl_2 and with 0.5, 1.0, or 2.0 equiv. of HCl-OEt_2.

Table 1. Fluorescence decay lifetimes of 2-quinolone in solution and in zeolite [a]

Condition	Lifetime (τ_i)/ns [b]			Preexponential factor (a_i)			Hamett acidity [c]
	τ_1	τ_2	τ_3	a_1	a_2	a_3	
CH_2Cl_2 [d]	0.16 (0.18) [g]			1.0			
EtOH [d]	0.16	0.42		0.69	0.31		
HCl/CH_2Cl_2 [e]	0.16	1.2		0.93	0.07		
BF_3/CH_2Cl_2 [f]	0.16	1.6 (1.6) [g]		0.79	0.21		
NaY	0.30	1.0		0.88	0.12		+3.3~+1.5
KL	0.33	1.1		0.94	0.06		+4.0~+3.3
HY	0.33	1.8		0.88	0.12		-3.0~-5.6
H-mordenite	0.32	2.3		0.88	0.12		-3.0~-5.6
H-ZSM-5	0.63	2.6	7.8	0.82	0.17	0.01	-5.6~-8.2

[a] The fluorescence decay lifetimes were determined by using a single photon counting apparatus reported in Reference 11. The decay curves were analyzed by using the equation, $I(t) = \Sigma a_i \exp(-t/\tau_i)$; excitation wavelength, 320 nm for solution and 330 nm for zeolite; emission wavelength, 373 nm. [b] Measured under air. [c] Determined by using Hammett indicators. [d] Data for Q = 1.0×10^{-4} M in the absence of HCl and BF_3. [e] Data for Q = 1.0×10^{-4} M in the presence of 2 equiv. of HCl-OEt_2. [f] Data for Q = 1.0×10^{-4} M in the presence of 2 equiv. of BF_3-OEt_2. [g] Lifetime reported in Reference 8.

Copyright © 1999 The Chemical Society of Japan

literature value of 0.18 ns.[8] In EtOH, two components with a significant difference in lifetime were observed, 0.16 ns (preexponential factor a = 0.69) and 0.42 ns (0.31), respectively. The species with the lifetime of 0.16 ns must be free Q and the 0.42 ns species is probably Q hydrogen-bonded with EtOH. In the presence of 2 equiv. of HCl, protonated Q with a lifetime of 1.2 ns (a = 0.07) was observed together with the 0.16 ns component (0.93).[7] As reported previously,[8] the lifetime of the Q-BF_3 complex was determined to be 1.6 ns (a = 0.21) under the present conditions. From these results, it is probable that the strength of interaction between Q and the Brønsted and Lewis acid sites in zeolites affects the fluorescence decay lifetime as in solution.

By using Hammett indicators, the acidity of the Brønsted acid sites in the zeolites was determined as shown in Table 1: NaY (Tosoh; pore size, 7.4 Å), +3.3~+1.5; KL (Tosoh; 7.1 Å), +4.0~+3.3; HY (Tosoh; 7.4 Å), -3.0~-5.6; H-mordenite (Tosoh; 7.0 x 6.5 Å), -3.0~-5.6; and H-ZSM-5 (Mizusawa Ind. Chem.; 5.3 x 5.4 and 5.1 x 5.5 Å), -5.6~-8.2. It should be noted that the change in the lifetime of Q included in the zeolites is related to the above acidity values. The major species in the zeolites had a lifetime of ca. 0.3 ns, except for H-ZSM-5, where a species with a longer lifetime (0.63 ns, a = 0.82) was predominant. It seems probable that the 0.3 ns species was stabilized Q or Q hydrogen-bonded with an OH group, in either case resulting from a process occurring in the cavities. The lifetimes of the other species observed depended on the Hammett acidity: for NaY and KL, the lifetimes (1.0 and 1.1 ns, respectively) are in close agreement with the lifetime of the Q-HCl complex in CH_2Cl_2. For HY, the second component (τ = 1.8 ns, a = 0.12) is probably due to stronger complexation at the Brønsted acid site than in the case of NaY and KL. It is notable that the second component for H-mordenite has a longer lifetime (τ = 2.3 ns) than that for HY, as in the case of H-ZSM-5 (2.6 ns). Therefore, although HY and H-mordenite showed similar Hammett acidity (-3.0~-5.6), it is likely that guest molecules included in the zeolites exhibit different chemical behavior: in fact, for *cis*- and *trans*-stilbenes, the formation of the dimer cation radical was observed in H-mordenite, but not in HY.[4]

On the basis of results reported recently,[1-5] ZSM-5 seems to be one of the most unique zeolites not only due to the fact that it has the strongest acidity but also because the pore size is suitable for a phenyl group, which has a considerable stabilizing effect on the reactive species generated and on the excited state of guest molecules. Indeed, the two components (0.63 and 2.6 ns, respectively) observed in the H-ZSM-5 cavity seem to be more stable compared to those in other zeolites. At the present time, we believe that the 0.63 ns species is highly stabilized or more strongly hydrogen-bonded Q, while the 2.6 ns species is the most stable Q-Brønsted acid complex formed in the zeolites used. In addition, the lifetime of a third species observed in H-ZSM-5 was determined to be 7.8 ns (a = 0.01). Because it was only in the Q/H-ZSM-5 sample that a radical species was detected by means of ESR spectroscopy, a cation radical of Q generated at the Lewis acid site might exist in the cavity, as in the case of stilbenes.[2-4]

Another notable feature of spectroscopic behavior was found by means of infrared (IR) absorption spectroscopy. As shown in Figure 2, the IR spectra of Q in CH_2Cl_2 changed significantly depending on the concentration: in the case of 10^{-1} M Q, absorption at 1660 cm^{-1} is stronger than at 1675 cm^{-1}, while the latter absorption becomes stronger at the concentration of 10^{-4} M. Accordingly, the band with the higher wavenumber has been attributed to non-hydrogen bonded Q, i.e. a monomer, and that with the lower wavenumber to a hydrogen-bonded dimer of Q.[9] Interestingly, IR spectra for the Q/zeolite samples also changed depending on the amount of Q loaded into the zeolites. For example, when most of the NaY cavities were occupied by Q, the spectrum was similar to that for 10^{-1} M Q in CH_2Cl_2; i.e. the strong absorption was observed at around 1650 cm^{-1}. In contrast, for NaY samples only partially loaded with Q, the 1650 cm^{-1} band shifted to the higher wavenumber side by ca. 50 cm^{-1}, which is attributable to a Q monomer. These results clearly indicate the possibility that the photochemical behavior of guest molecules included in zeolites is controlled by the amount of Q loaded.[12] Furthermore, it was found that IR spectra for Q adsorbed on silica gel (Catalysis Society of Japan, JRC-SIO-5) and silica-alumina (Nikki Chem. Co., N631-L) very closely resemble the spectra for the NaY samples, again depending on the amount of Q adsorbed on the surface.

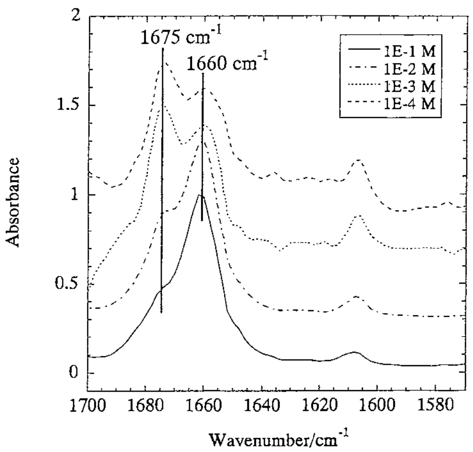


Figure 2. Concentration dependent IR spectra of 2-quinolone in CH_2Cl_2: 10^{-1} M, 10^{-2} M, 10^{-3} M, and 10^{-4} M.

Finally, we conclude that the present results characterize several commercially obtainable zeolites on the basis of the spectroscopic and photophysical data for the ground- and excited-state guest molecule Q and also suggest that it is highly likely that Q included in zeolites exhibits different photochemical behavior from that in solution.

References

1 a) "Surface Photochemistry," ed by M. Anpo, Wiley, Chichester (1996), Vol. 1. b) "Photochemistry in Organized and Constrained Media," ed by V. Ramamurthy, VCH, New York (1991).
2 V. Ramamurthy, J. V. Casper, and D. R. Corbin, *J. Am. Chem. Soc.*, **113**, 594 (1991).
3 X. Liu, K.-K. Iu, J. K. Thomas, H. He, and J. Klinowski, *J. Am. Chem. Soc.*, **116**, 11811 (1994).
4 M. Kojima, H. Takeya, Y. Kuriyama, and S. Oishi, *Chem. Lett.*, **1997**, 997.
5 V. J. Rao, N. Prevost, V. Ramamurthy, M. Kojima, and L. J. Johnston, *J. Chem. Soc., Chem. Commun.*, **1997**, 2209.
6 C. Matsubara and M. Kojima, *Tetrahedron Lett.*, **40**, 3439 (1999).
7 a) S. G. Schulman, A. C. Capomacchia, and B. Tussey, *Photochem. Photobiol.*, **14**, 733 (1971). b) S. G. Schulman and B. S. Vogt, *J. Phys. Chem.*, **85**, 2074 (1981).
8 F. D. Lewis, G. D. Reddy, J. E. Elbert, B. E. Tillberg, J. A. Meltzer, and M. Kojima, *J. Org. Chem.*, **56**, 5311 (1991).
9 J. C. Petersen, *J. Phys. Chem.*, **75**, 1129 (1971).
10 M. Kido and K. Nakagawa, *Chem. Pharm. Bull.*, **30**, 1488 (1982).
11 H. Satozono, S. Suzuki, N. Tokou, H. Takehara, and Y. Uno, *Nippon Kagaku Kaishi* (*J. Chem. Soc. Jpn., Chem. Indus. Chem.*), **1994**, 115.
12 S. L. Suib and A. Kostapapas, *J. Am. Chem. Soc.*, **106**, 7705 (1984).