CHEMISTRY LETTERS, pp.1107-1108, 1977. Published by the Chemical Society of Japan

QUENCHING EFFECT OF OXIMES ON THE PHOTOLYSIS OF COPOLYMER OF STYRENE AND PHENYL VINYL KETONE[1)]

Masahiro TSUNOOKA, Todomu NISHINO, and Makoto TANAKA
Department of Applied Chemistry, Faculty of Engineering, University of Osaka Prefecture, Sakai City, Osaka 591

In order to estimate the function of oximes as quenchers, their effect on the photolysis of copolymer of styrene and phenyl vinyl ketone was investigated in solution and in the solid phase. 2-Acetonaphthone oxime and benzylidene acetone oxime among the oximes examined in this paper were as effective as naphthalene, which is a well known quencher.

It is known that excited azomethine compounds are apt to decay to the ground state because of rotation about the π bond in the excited state.[2)] This suggests that azomethine compounds act as quenchers of photochemical reactions. In this paper, in order to investigate the behavior of oximes as quenchers the photolyses of copolymer of styrene and phenyl vinyl ketone(Co-St-PVK) in the presence of oximes were carried out in solution and in the solid phase.

Co-St-PVK having 7 mol % phenyl vinyl ketone and the degree of polymerization of 1300 was used. The photolysis of Co-St-PVK in a benzene solution was carried out in a cylindrical Pyrex cell under air. A Toshiba SHL 100 UV high pressure mercury lamp was used as the light source and the 366 nm line was isolated by means of a Toshiba UVD1B filter. From the change of molecular weight of the copolymer before and after irradiation, which was determined viscometrically, the number of scission was calculated. For the Stern-Volmer plots and the Perrin plots, the ratio of the scission numbers in the absence and presence of oximes was taken as the ratio of quantum yields(ϕ_0/ϕ). Oximes used as quenchers were 2-acetonaphthone oxime(2-ANO), benzylidene acetone oxime(BAO), benzophenone oxime(BPO) and actophenone oxime(APO). The photolysis in the solid phase was carried out by irradiating the film of the copolymer under air, which was prepared from a benzene solution.

(1) Photolysis in solution. The quantum yields for the scission of Co-St-PVK decreased by adding oximes and the relationships between ϕ_0/ϕ and the concentration of oxime showed straight lines. This means that oximes act triplet quenchers, because the copolymer has been known to photolyze via triplet state.[3)] The Stern-Volmer constants($K_q\tau$) determined from the slopes were shown in Table 1. For comparison, the $k_q\tau$ values for ferrocene and naphthalene, which were well known as triplet quenchers for the copolymer, were shown. The $k_q\tau$ values were divided into two groups: the one having $k_q\tau$ about 180 and the other having $k_q\tau$ less than 180. In the photolysis of butyrophenone, naphthalene is known to be a "diffusion controlled" quencher.[4)] Therefore, BAO, 2-ANO and ferrocene the $k_q\tau$ values of which are similar to that of naphthalene are thought to be diffusion controlled quenchers.

2) Photolysis in the solid phase. Hrdlovic et al.[5] used the Stern-Volmer constant for comparison of the quenching efficiency of many organic compounds in the photodegradation of poly(phenyl vinyl ketone) film. However, the Stern-Volmer plots for some quenchers did not show straight lines. The present Stern-Volmer plots for oximes as quenchers were also appreciably curved and consequently the estimation of $k_q\tau$ value was impossible.

Perrin proposed the following equation for the energy transfer in the solid phase:[6] $\phi_0/\phi = \exp(VN[Q])$, $V = (4/3)\pi R_0^3$ where ϕ_0/ϕ were the ratio of the phosphorescence yields of an excited donor in the absence and presence of an acceptor, respectively. V, N, Q and R_0 represent the volume of a quenching sphere, Avogadro's number, the concentration of the acceptor and the radius of the sphere, respectively. In the present experiment, the scission number of the copolymer was used instead of the phosphorescence yield. The plots of $\log(\phi_0/\phi)$ against the concentration of oxime gave straight lines through the origin, showing that the Perrin equation could be applied to the present photolysis. As shown in Table 2, the radii obtained from the slopes were about 11 Å, suggesting that this quenching reaction proceeded via an exchange mechanism.[7] The quenching radius of APO which was less effective in solution, was a little smaller than those of the others.

Table 1. Stern-Volmer constants for the quenching of the photolysis of Co-St-PVK by oxime in benzene at 30 °C

Quencher	$k_q\tau$ (l/mol)
BAO	184
2-ANO	179
Ferrocene	180*
Naphthalene	183
BPO	78
APO	76

* The value was corrected for screening effect.

Table 2. Quenching of Photolysis of Co-St-PVK film by oxime at room temperature

Quencher	R_0 (A)
BAO	11.8
2-ANO	11.4
Ferrocene	11.3*
Naphthalene	11.3
APO	10.6

* The value was corrected for screening effect.

References

1) Photochemical Reactions of High Polymers XVI. Preceding paper: M.Tsunooka, Y.Itami, Y.Higashi and M.Tanaka, submitted for publication in Bull. Chem. Soc. Jpn.
2) A.Padwa and J.Smolanoff, J.Am. Chem. Soc., 93, 548 (1971).
3) F.J.Golemba and J.E.Guillet, Macromolecule, 5, 212 (1972).
4) P.J.Wagner, J.Am. Chem. Soc., 89, 2820 (1967).
5) P.Hrdlovic, I.Lukac and Z.Manasek, Chem. Zvesti., 26, 433 (1972).
6) F.Perrin, Compt. Rend., 178, 1978 (1924).
7) N.J.Turro, "Molecular Photochemistry", W.A.Benjamin, Inc., New York (1965), p108.

(Received July 9, 1977)