BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 695—696 (1973)

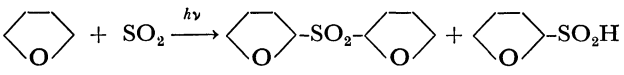
The Photochemical Reactions of Tetrahydrofuran and Tetrahydrothiophene with Sulfur Dioxide

Hiroshi Takeuchi*, Toshikazu Nagai**, and Niichiro Tokura
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Yamada-kami, Osaka

(Received May 29, 1972)

The reaction of photochemically-excited sulfur dioxide (SO_2) with paraffins and olefins has been studied by a number of investigators.$^{1-7)}$ Calvert and his co-workers$^{6,7)}$ concluded that the excited triplet SO_2 molecule is the most important reactant leading to the product formation in the above systems. Though Dainton and Ivin$^{1)}$ thought that sulfinic acids are the main products of the above reactions, there was no assurance that the products were thermally-unstable sulfinic acids. Dunken and Winde$^{8,9)}$ reported the formation of a charge-transfer complex between ether and SO_2. We have initiated studies aimed at the confirmation of the photochemical products in the reaction of tetrahydrofuran (THF) with SO_2.

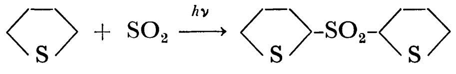
In the dark, no product was formed in the system of THF and SO_2, but a photochemical reaction in the above system yielded two new compounds, di-2-tetrahydrofurylsulfone (I) and 2-tetrahydrofuransulfinic acid (II). Since these products were unstable under atmospheric conditions, they were confirmed by the method to be described in the experimental section.



(I) (II)

The results are indicated in Table 1. The formation of I and II was observed in experiments using various irradiation sources under both degassed and aerial conditions.

The experiment using tetrahydrothiophene (THT) in place of THF was carried out to see if sulfone or sulfinic acid could be formed. The new compound, di-2-tetrahydrothiophenylsulfone (IV), was obtained in a low yield. In this reaction, the formation of sulfinic acid could not be observed. The mechanism of this reaction is ambiguous, but one possible explanation of the low reactivity of THT with SO_2 may depend upon the more reactive C–H bond at the transition state in the reaction of THF with SO_2 in comparison with the C–H bond in that of THT with SO_2.



(IV)

Since the products, I, II, and IV, were formed by the selective reactions of SO_2 at the 2-positions of THF and THT, these ractions were interesting synthetically.

Experimental

A solution of THF and SO_2 in a quartz pressure-vessel was irradiated at 0°C under the conditions shown in Table 1. The solvent was distilled under reduced pressure, and the residue was recrystallized from cyclohexane to give di-2-tetrahydrofurylsulfone (I) (mp 68—70°C). Since product I was unstable under atmospheric conditions, it was immediately analyzed after drying under a vacuum. IR (Nujol):

Table 1. Photochemical reaction of THF with SO_2

THF (g)	SO_2 (g)	Surrounding conditions	Irradiation source$^{a)}$	Irradiation time (hr)	Products (g)	
					I	Anilinium salt of II
106	42	Degassed	H 600 W	10	12.3	—
102	41	Degassed	H 300 W	15	8.6	3.7
80.5	24.5	Aerial	H 300 W$^{b)}$	10.5	3.5	0.9
130	46.5	Aerial	H 600 W	10	12.3	—
98	38.7	Aerial	H 600 W	5	2.7	13.5
89	35.1	Degassed	L 120 W	23	2.7	7.5

a) H: High-pressure mercury lamp. L: Low pressure mercury lamp. b) Use of a Pyrex filter.

---

* Present address: Department of Synthetic Chemistry, Faculty of Engineering, Shinshu University, Wakazato, Nagano.

** Present address: College of General Education, Osaka University, Toyonaka, Osaka.

1) a) F. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.*, **46**, 374 (1950). b) F. S. Dainton and K. J. Ivin, *ibid.*, **46**, 382 (1950).

2) H. S. Johnston and K. D. Jain, *Science*, **131**, 1523 (1960).

3) Y. Ogata, Y. Izawa, and T. Tsuda, *Tetrahedron*, **21**, 1349 (1965).

4) Y. Ogata, Y. Izawa, and T. Tsuda, This Bulletin, **38**, 1984 (1965).

5) R. B. Timmons, *Photochem. Photobiol.*, **12**, 219 (1970).

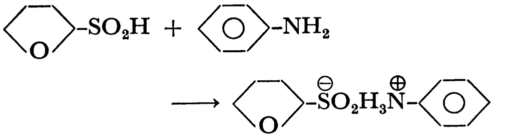
6) C. C. Badcock, H. W. Sidebottom, J. G. Calvert, G. W. Reinhardt, and E. K. Damon, *J. Amer. Chem. Soc.*, **93**, 3115 (1971).

7) H. W. Sidebottom, C. C. Badcock, J. G. Calvert, B. R. Rabe, and E. K. Damon, *ibid.*, **93**, 3121 (1971).

8) H. Dunken and H. Winde, *Z. Physik. Chem.*, **56**, 303 (1967).

9) H. Dunken and H. Winde, *ibid.*, **58**, 246 (1968).

1140 and 1310 cm^{-1} (ν_{SO_2}), and 1060 cm^{-1} (ν_{C-O}); NMR in CCl_4 (τ): 4.8—5.1 (m, 2H, methine), 5.7—6.2 (m, 4H, $-OCH_2-$), and 7.4—8.3 (m, 8H, methylene); Found: C, 46.47; H, 6.92%; mol wt, 211 (by the vapor-pressure method) and 206 (by hydrolysis using aqueous *ca.* 0.3 N NaOH). Calcd for $C_8H_{14}O_4S$: C, 46.58; H, 6.84;% mol wt, 206.3. Mass spectrum: *m/e*; 188 (M^+-H_2O), 96, 70 (dihydrofuran$^{+\cdot}$), 64 ($\overset{+\cdot}{S}O_2$), 48 ($\overset{+\cdot}{S}O$), 41, and 39 (the cyclopropenium ion). The residue obtained after the separation of I was neutralized with aniline. The precipitate which there upon appeared was filtered off and crystallized from benzene to give an anilinium salt of 2-tetrahydrofuransulfinic acid (II), Compound III (mp 102—104°C). After it had been dried under a vacuum, the structure of III was



(III)

confirmed from the following data. IR (Nujol): 940 and 1020 cm^{-1} ($\nu_{\overset{\ominus}{S}O_2}$), and 1500 and 1610 cm^{-1} ($\nu_{\overset{\oplus}{N}H_3}$); NMR in $CDCl_3$ (τ): 1.6 (s, 3H, $-\overset{+}{N}H_3$), 2.7—2.9 (m, 5H, aromatic), 5.8—6.05 (t, *J*=3 Hz, 1H, methine), 6.1—6.4 (t, *J*=6 Hz, 2H, $-OCH_2-$), and 7.7—8.4 (m, 4H, methylene); Mass spectrum: *m/e*; 93 ($Ph\overset{+\cdot}{N}H_2$), 70 (dihydrofuran$^{+\cdot}$), 64 ($\overset{+\cdot}{S}O_2$), and 48 ($\overset{+\cdot}{S}O_2$); Found: C, 52.27; H, 6.53; N, 6.21%. Calcd for $C_{10}H_{15}NO_3S$: C, 52.38; H, 6.59; N, 6.11%. The neutralization equivalent was determined with NaOH in an aqueous solution; Found: 220. Calcd: 229.3.

A solution of THT (100 g) and SO_2 (24 g) in a quartz pressure vessel was irradiated by a high-pressure mercury lamp (600 W) for 7 hr at 0°C under degassed conditions. Di-2-tetrahydrothiophenylsulfone (IV) was thus obtained in a low yield (85 mg); mp 137—139°C (recrystallized from methanol). Th structure of IV was confirmed from the following data. IR (Nujol): 1130 and 1300 cm^{-1} (ν_{SO_2}); NMR in $CDCl_3$ (τ): 4.9—5.15 (m, 2H, methine), 6.8—7.15 (m, 4H, $-CH_2S-$), and 7.2—8.0 (m, 8H, methylene); Found: C, 40.35; H, 5.71%. Calcd for $C_8H_{14}O_2S_3$: C, 40.31; H, 5.92%. Mass spectrum: *m/e*; 238 (M^+), 174 (M^+-SO_2), 87, 86 (dihydrothiophene$^{+\cdot}$), 64 ($\overset{+\cdot}{S}O_2$), 59, 58, 53, and 45 ($^+S{\equiv}CH$).