22. Pyrolysis of N-Sulfinylaniline
Microwave Detection of the SO Molecule

Preliminary communication[1])

by Shuji Saito

Sagami Chemical Research Center
Sagamihara, Kanagawa, 229, Japan

and Curt Wentrup

Institut de Chimie Organique, Université de Lausanne, Switzerland

(3. XII. 70)

*Summary.* Gas-phase pyrolysis of N-sulfinylaniline at 650–980°C produces SO ($^3\Sigma^-$), identified by its rotational line, $J, K = 2,1 \leftarrow 1,0$ in the microwave spectrum, increasing in intensity with the temperature. SO_2 was observed with a parallel absorption intensity in the same temperature interval; its partial pressure was determined as *ca.* 8% at 980°. The results confirm the dissociation of N-sulfinylaniline into phenylnitrene and sulfur monoxide.

It was reported previously [1] that phenylnitrene, formed by decomposition of phenyl azide, undergoes two kinds of reaction, *viz.* ring contraction to 1-cyanocyclopentadiene, and hydrogen abstraction or dimerization to form aniline and azobenzene. It was considered that the former reaction involves phenylnitrene in the initially generated singlet state, the latter in the triplet state, produced by spin inversion. More recently, it was found [2] that N-sulfinylaniline gives pyrolysis products similar to those above. This suggested that N-sulfinylaniline decomposes into phenylnitrene and SO, though sulfur monoxide had not been identified in the reaction by any analytical method. It was of particular importance to know in which electronic states phenylnitrene and SO were initially generated.

Saito [3] has confirmed the existence of the SO($^3\Sigma^-$) molecule in the pyrolysis products of ethylene episulfoxide by microwave spectroscopy, and discussed the mechanism of its formation with special reference to the electronic states of the ethylene and SO generated. In this connection, it must be noted that a rotational transition, $J = 3 \leftarrow 2$ of the SO molecule in the $^1\Delta$ state has been detected by microwave spectroscopy [4]. The main purpose of the present work was to determine whether the SO molecule is really generated in the thermal decomposition of N-sulfinylaniline.

The pyrolysis was carried out in a quartz tube of 11 mm diameter. The decomposition products were led for analysis into the parallel plate absorption cell of a conventional microwave spectrometer of high sensitivity with 100 kHz *Stark* modulation [5]. The distance between the absorption cell and the reaction tube was about 10 cm. When the temperature of the quartz tube was raised gradually under the flow of N-sulfinylaniline at 0.04 Torr, a rotational line of sulfur monoxide in the $^3\Sigma^-$ ground state, $J, K = 2.1 \leftarrow 1.0$ at 62931.0 MHz [6] was observed on a crystal rectifier-oscilloscope at about 650°C. The peak intensity increased, as shown in the Figure,

---

[1]) The full paper will probably be published in Helv.
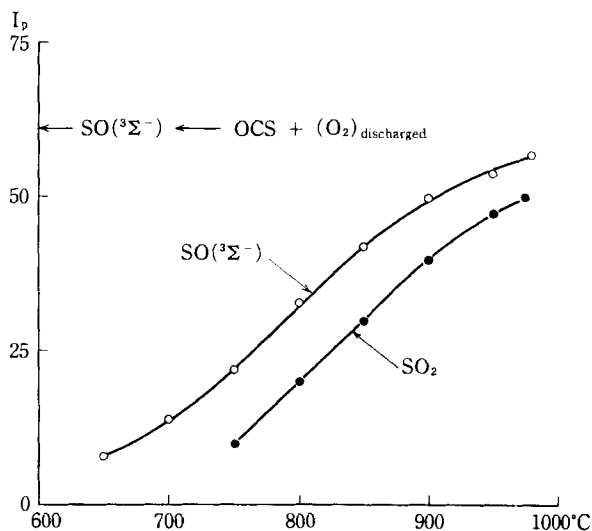
Temperature variation of the absorption peak intensities of SO $(^3\Sigma^-)$ *and* SO$_2$. *(I_p in an arbitrary unit)*

above 650 °C. At 980 °C, the highest temperature available, the peak intensity of the absorption line for SO($^3\Sigma^-$) was comparable with that of SO($^3\Sigma^-$) formed by the reaction:

$$OCS + (O_2)_{discharged} \rightarrow SO(^3\Sigma^-) \,.$$

A rotational line of SO$_2$, $31_{5,27} \leftarrow 30_{6,24}$ at 47660.99 MHz [7] was also observed in the pyrolysis products, as in the thermal decomposition of ethylene episulfoxide. The intensity of the transition showed a temperature variation similar to that of SO($^3\Sigma^-$), as is also indicated in the Figure. At 980 °C the partial pressure of SO$_2$ was determined to be *ca.* 8% by a semi-quantitative analysis. SO$_2$ was also identified by its mass spectrum [2].

These results confirm that 1-cyanocyclopentadiene and at least some of the aniline isolated from the pyrolysis mixture [2] are derived from phenylnitrene, which in turn is formed by elimination of SO from N-sulfinylaniline. At present, it may be said that the sulfur monoxide molecule in the $^3\Sigma^-$ state must be formed by one or both of the following reactions:
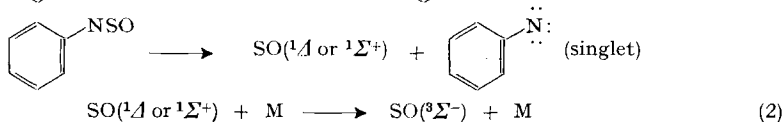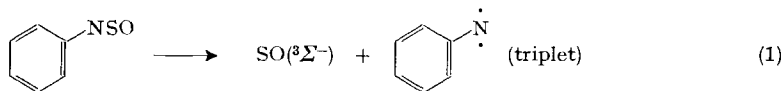
Detection of the sulfur monoxide molecule in the $^1\Delta$ state was not attempted because it seemed impossible that it could survive to the absorption cell, even if it were formed initially in that state. Further experiments now in progress, using a high temperature absorption cell, may distinguish between the reactions (1) and (2).

BIBLIOGRAPHY

[1] *W. D. Crow* & *C. Wentrup*, Tetrahedron Letters *1967*, 4379.

[2] *C. Wentrup*, Tetrahedron *1971*, in press.

[3] *S. Saito*, Tetrahedron Letters *1968*, 4961; Bull. chem. Soc. Japan *42*, 667 (1969).

[4] *S. Saito*, J. chem. Physics *53*, 2544 (1970).

[5] *S. Saito* & *T. Amano*, J. molec. Spectroscopy *34*, 383 (1970).

[6] *F. X. Powell* & *D. R. Lide, Jr.*, J. chem. Physics *41*, 1413 (1964).

[7] *A. Bauer* & *J. Bellet*, C. r. hebd. Séances Acad. Sci. *258*, 873 (1964).

23. Organische Phosphorverbindungen 44

Darstellung und Eigenschaften von Bis-(β-chloräthyl)-phosphinsäure-Derivaten [1][1])
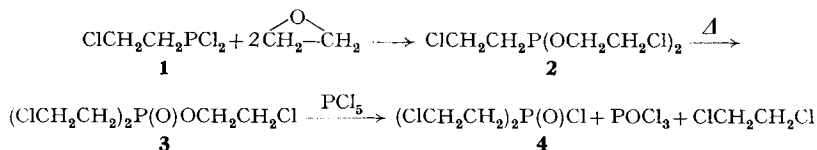
von Ludwig Maier

Monsanto Research S. A., 8050 Zürich, Eggbühlstrasse 36

(4. XII. 70)

Summary. Reaction of $ClCH_2CH_2PCl_2$ with ethylene oxide gives the phosphonous acid ester $ClCH_2CH_2P(OCH_2CH_2Cl)_2$ which on heating to 120° rearranges to the phosphinic acid ester $(ClCH_2CH_2)_2P(O)OCH_2CH_2Cl$ (3). Chlorination of 3 with PCl_5 in CCl_4-solution yields the phosphinic chloride $(ClCH_2CH_2)P(O)Cl$ (4), which on treatment with P_2S_5 at 170° produces the thio-derivative, $(ClCH_2CH_2)_2P(S)Cl$, (5). Treatment of 4 and 5 with alcohols, mercaptanes, or amines in the presence of an acid binding agent leads to the corresponding phosphinic and thiophosphinic acid derivatives, $(ClCH_2CH_2)P(X)Y$, (X = O, S; Y = OR, SR, NR_2) (6). Reaction of 6 with excess base yields the corresponding divinylphosphinic and divinylthiophosphinic acid derivatives $(CH_2=CH)_2P(X)Y$ (X = O, S; Y = OR, SR, NR_2) (7).

Bis-(β-chloroethyl)-phosphinates, *e.g.* $(ClCH_2CH_2)_2P(O)OEt$, undergo a *Michaelis-Arbuzov* reaction when heated with phosphites to 160–170° to give bis-(phosphonylethyl)-phosphinates, *e.g.* $(EtO)(O)P[CH_2CH_2P(O)(OEt)_2]_2$ (8), which on hydrolysis with conc. HCl under reflux yield the corresponding acid $HO_2P(CH_2CH_2PO_3H_2)_2$.

Behandlung von β-Chloräthyl-dichlorphosphin (1) [2] mit Äthylenoxid führt in 93% Ausbeute zum Phosphonit 2, ein farbloses Öl, ^{31}P-chem. Verschiebung −179,5 ppm. Erhitzen von 2 auf 120° für 5 Std. gibt in einer intramolekularen *Michaelis-Arbuzov*-Umlagerung in 96% Ausbeute Bis-(βchloräthyl)-phosphinat (3), ein farbloses, viskoses Öl, ^{31}P-chem. Verschiebung: − 49,6 ppm. Chlorierung des Phosphinates

$$ClCH_2CH_2PCl_2 + 2\ \overset{O}{\overset{\frown}{CH_2-CH_2}} \longrightarrow ClCH_2CH_2P(OCH_2CH_2Cl)_2 \xrightarrow{\ \Delta\ }$$
$$\mathbf{1} \qquad\qquad\qquad\qquad\qquad \mathbf{2}$$

$$(ClCH_2CH_2)_2P(O)OCH_2CH_2Cl \xrightarrow{\ PCl_5\ } (ClCH_2CH_2)_2P(O)Cl + POCl_3 + ClCH_2CH_2Cl$$
$$\mathbf{3} \qquad\qquad\qquad\qquad\qquad\qquad \mathbf{4}$$

3 mit PCl_5 in CCl_4-Lösung liefert Bis-(β-chloräthyl)-phosphinsäurechlorid (4), Sdp. 113–5°/0,01 Torr, Smp. 32–33°, ^{31}P-chem. Verschiebung: − 60,3 ppm (in $CHCl_3$). Beim Erhitzen von 4 mit P_2S_5 für 4 Std. auf 170° wird Bis-(β-chloräthyl)-thiophosphinsäure-

---

[1]) Alle in dieser Arbeit angeführten neuen Verbindungen gaben bei der Elementaranalyse die richtigen Werte.