React. Kinet. Catal. Lett., Vol. 19, No. 3–4, 383–387 (1982)

PHOTOLYSIS OF SO_2-ALKANE-NO SYSTEMS IN THE GAS PHASE

T. A. Andreeva*, V. I. Makarov, G. I. Skubnevskaya and N. M. Bazhin

*Institute of Inorganic Chemistry, Kemerovo,
Institute of Chemical Kinetics and Combustion, Novosibirsk, USSR

Received October 15, 1981
Accepted November 27, 1981

The photolysis products of SO_2-pentane-NO mixtures are N_2O, H_2O and a compound designated as RNO. Kinetic data obtained by GC method confirm the previously proposed scheme of photolysis. Also studied was the photolysis of SO_2, NO and cyclohexane mixtures. From comparison of spectral characteristics of RNO and its analog 2-methyl-2-nitrosopropane, the probable structure of RNO is suggested.

При фотолизе смесей SO_2-пентан-NO зарегистрированы продукты N_2O, H_2O и смесь, обозначенная как RNO. Кинетические данные, полученные методом ГХ, подтвердили ранее предложенную схему фотолиза. Изучен также фотолиз смеси SO_2 и NO с циклогексаном. Сопоставление спектральных характеристик RNO и предполагаемого аналога 2-метил-2-нитрозопропана позволило высказать предпожения о структуре RNO.

The kinetics and mechanism of SO_2-alkane photolysis have been extensively discussed in view of its contribution to photochemical smog formation /1/. Besides sulfinic acids /2/, such products as sulfonic acids, sulfones, etc. were detected /3/. An attempt has been made to detect these compounds in the city atmosphere /4/.

Nitrogen oxides often accompany SO_2 and alkanes in air-polluting gases. Since the presence of NO prevents mist formation /5/, it was assumed to quench the reactive triplet state of SO_2, thus inhibiting the reaction. Our UV-spectroscopic studies of SO_2-pentane-NO photolysis indicated that NO also actively enters into secondary reactions and this is the reason for the effective NO-induced inhibition of aerosol formation /6, 7/.

In the present work, to study the initial photolysis step in more detail, we have used a gas chromatographic technique (GC).

Table 1
Gas chromatography conditions

Carrier	T (K)		C_5H_{12}		SO_2	
	evapor.	column	t	sensitivity	t	sensitivity
POLYSORB-1	423	373	282[a]	0.5[b]	56	0.35
CHROMOTZVET with 2% squalane	373	343	300	15[c]	–	–
CHROMATON with 15% polyethylene + POLYSORB-1	373	343	63	18	111	15
SILICA	423	313	276	5.8	–	–

Carrier	T (K)		NO		N_2O	
	evapor.	column	t	sensitivity	t	sensitivity
POLYSORB-1	423	373	30	0.2	–	–
CHROMOTZVET with 2% squalane	373	343	90	16	–	–
CHROMATON with 15% polyethylene + POLYSORB-1	373	343	45	21.5	–	–
SILICA	423	313	27	23.5	42	18

[a] t – elution time (s),
[b] Peak area (cm^2/Torr) at V = 600 mm/h.
[c] Intensity of peak (mm/Torr)

The preparation of NO and SO_2 gases and the experimental conditions were described elsewhere /6, 7/. The GC analysis was performed on an LHM-8MD chromatograph with a catharometer as a detector. The carrier gas was helium (99.985 %, 60 ml/min flow rate). GC recording conditions are listed in Table 1.

The data obtained refer to the initial photolysis step when the SO_2 concentration is unchanged and the NO and pentane contents decrease linearly with the time (Fig. 1). The ratio of the slopes of NO and pentane consumption is equal to 2.1±0.3, which confirms the reaction scheme /7, 8/ according to which, the initial step is C–H bond dissociation:

$$SO_2 \xrightarrow{h\nu} SO_2^x \tag{1}$$

$$SO_2^x + RH \longrightarrow \dot{R} + H\dot{S}O_2 \tag{2}$$

Then one NO molecule is added to $\dot{R}$ yielding the supposed product RNO, and the other substitutes SO_2 in $H\dot{S}O_2$ radical yielding HNO:

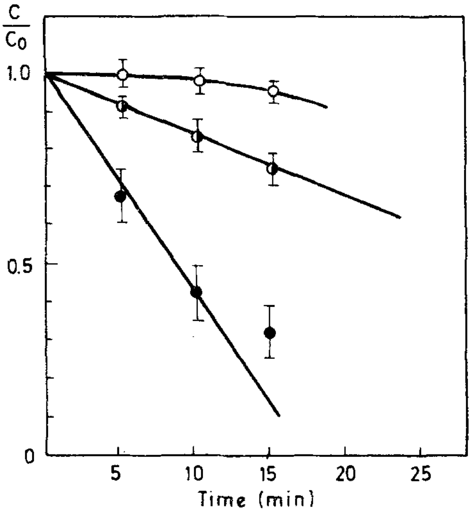

Fig. 1. Variations of the relative concentration (C/C_0) in SO_2-n-pentane-NO photolysis calculated from chromatographic data (○) – SO_2, (●) – pentane, (●) – NO. $P_{SO_2} : P_{RH} : P_{NO} = 1 : 1 : 0.38$, $P_{total} = 5–15$ Torr

$$\dot{R} + NO \longrightarrow RNO \tag{3}$$

$$H\dot{S}O_2 + NO \longrightarrow HNO + SO_2 \tag{4}$$

As is known /9/, the fastest process of further HNO transformations is the reaction

$$2HNO \longrightarrow N_2O + H_2O \tag{5}$$

N_2O and H_2O were detected after photolysis by GC. However, a quantitative agreement with the scheme appeared impossible since HNO decays heterogeneously on the walls /10/.

The gaseous RNO gradually deposits on the walls, which can be proved by the decreasing intensity of its UV spectrum. The deposited product is soluble in water, alcohol and less soluble in CCl_4. The product referred to as RNO, can be a mixture of initial and the secondary nitroso compounds. Moreover, aliphatic nitroso compounds are characterized by isomerization to oximes /11/. The IR-spectrum of RNO in CCl_4 solution has no intense band at 3400 cm^{-1} characteristic for the OH vibration of oximes /12/. Its NMR spectrum exhibits no peak in the 7–11 ppm region where the oxime proton is usually observed /13/. These results indicate

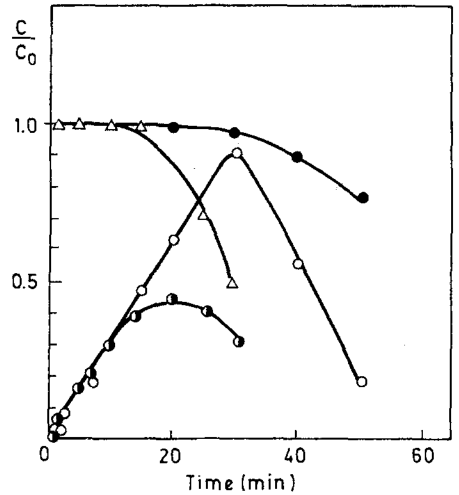

Fig. 2. Yields of photolysis products (○, ◑), and SO_2 consumption (△, ●) in SO_2-n-pentane-NO (○, ●) and SO_2-cyclohexane-NO (△, ◑) mixtures vs. time according to UV spectroscopy data

that the product RNO is not an oxime in accordance with Refs. /14, 15/, where the nitroso isomer of RNO was assumed to stabilize with increasing molecular weight of alkane.

Spectral characteristics of RNO were compared with its assumed analog 2-methyl-2-nitrosopropane (MNP). A monomer $\rightleftharpoons$ dimer equilibrium can take place in the RNO solution /11/. A peak at 1560 cm^{-1} is observed in the IR spectra of both RNO and MNP, corresponding to a monomeric nitroso group /11, 12/. The absorption intensity at 1560 cm^{-1} falls in both RNO and MNP films, formed by evaporation of the solvent. However, there appears an IR band at 1100 cm^{-1}, which can be attributed to the C–N vibrations of the nitroso group. UV spectra of gaseous RNO and MNP exhibit an absorption band in the same region as for aliphatic nitrosoalkanes /11, 14/. The maximum UV absorption is observed at 33 000 cm^{-1} for both RNO and MNP in CCl_4 solution and corresponds to a nitroso dimer.

The above data cannot give an unambiguous answer about the structure of the photolysis product RNO. It may be assumed that one of the products is nitrosoalkane, others can be the results of secondary reactions.

To elucidate the product composition we have studied the kinetics of the photolysis of SO_2-cyclohexane-NO and SO_2–CF_3H–NO mixtures. The reaction product with cyclohexane was found to be less stable than with pentane (Fig. 2), while with trifluoromethane the photolysis proceeds extremely slowly.

Thus the additional results obtained in the present study confirm the earlier scheme of SO_2–RH–NO photolysis /6, 7/.

The authors are thankful to L. Ya. Gavrilina and B. Z. Gorbunov for fruitful discussions.

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