SHORT COMMUNICATIONS

ICE NUCLEATING ABILITY OF METEORITIC MATERIAL

M. Munir Qureshi

Dawood College of Engineering and Technology, Karachi

J. Maybank

Physics Division, Saskatchewan Research Council, Saskatoon, Canada

(Received October 18, 1966)

Introduction

While investigating the ability of meteoritic material as rainforming nuclei, Qureshi and Maybank,[1] using mixing cloud chamber technique, made tests on thirteen samples of different meteorites. These comprised six samples of iron-nickle type (siderites), five samples of stony type (aerolites) and two samples of the intermediate variety (siderolites). They found that two of the thirteen samples tested—one siderite (S-6) and the other an aerolite (A-3)—had threshold temperatures for the onset of ice nucleation activity higher than -15°c. On the basis of this arbitrary division, these samples were considered as slightly active sources of ice nuclei, although not so effective as such soil components as kaolinite and halloysite (Mason and Maybank[2] and Mason).[3] The other eleven specimens were classified as relatively ineffective ice nucleators.

Experimental and Conclusion

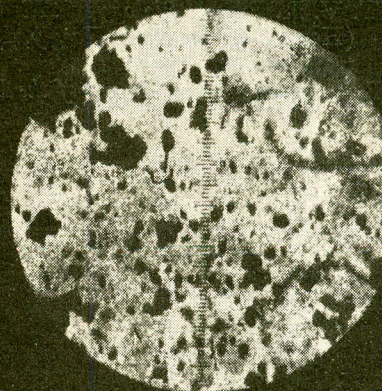In order to ascribe the possible cause for this different behaviour among the different meteo-
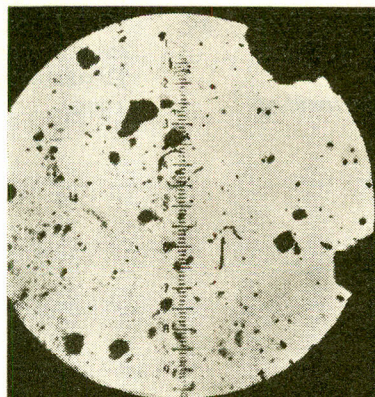
Fig. 1.—Photomicrographs of pulverisded meteoritic material used in the nucleation tests (magnification 2.7 μ per small scale division).

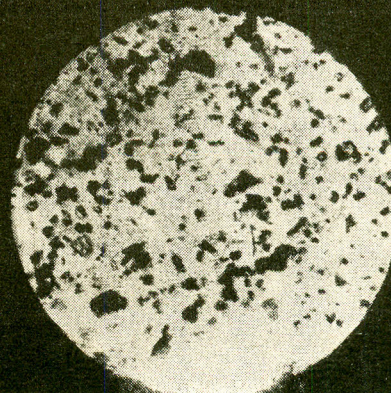(a) Inactive siderite (S-5)

(b) Siderite, active at —14.0°C (S-6)

(c) Inactive aerolite (A-1)

(d) Aerolite, active at —13.0°C (A-3)

rites, the photomicrographs (magnification 2.7μ per small division) of the two active samples, viz. S-6 and A-3, and the two most inactive samples, viz. S-5 and A-1, all crushed to micron-sized particles, were taken (Fig. 1). The photomicrographs illustrated the particle size and shape of the samples. From a close examination of the photomicrographs it would appear that the two active meteoritic specimens contained rather large fraction of quite angular particles (Figs. 1b and 1d). These are not present in the other two pictures (Figs. 1a and 1c) showing samples of two inactive specimens. No other reason for the different results obtained is apparent from this work at the present time.

References

1. M. Munir Qureshi and J. Maybank, Nature, **211**, 508, (1966).
2. B. J. Mason and J. Maybank, Quart. J. Roy. Met. Soc., **84**, 235 (1958).
3. B. J. Mason, Quart J. Roy. Met. Soc. **86**, 552 (1960).

KINETICS AND MECHANISM OF SULPHOXIDE OXIDATIONS, SOLVENT-EFFECTS IN THE OXIDATION OF DIPHENYL SULPHOXIDE WITH PEROXYBENZOIC ACID

SHAFIQ AHMAD KHAN and MUHAMMAD ASHRAF

West Regional Laboratories, Pakistan Council of Scientific and Industrial Research, Lahore

Introduction

It was pointed out in our previous work that the rate constants for the oxidation of sulphoxides with peroxybenzoic acid may have a relationship with the polarity of the solvents. This observation was based on the fact that the rates of oxidation of certain aromatic sulphoxides decrease considerably when the solvent was changed from toluene to acetone and then to methanol.[1] It was, therefore, considered appropriate to investigate this aspect in detail employing solvents with large variations in their dielectric constants. The present studies were thus started with a view to establishing or otherwise the relationship, if any, between such solvent properties and the rate of the sulphoxide oxidation reactions. Since the oxidation behaviour of sulphoxide from the kinetic point of view had not so far been thoroughly investigated, such a study was essentially called for. The oxidation of diphenyl sulphoxide with peroxybenzoic acid was, therefore, studied in cyclohexane, benzene, toluene, n-propanol, acetone, methanol and acetonitrile (the solvents are given in the ascending order of their dielectric constants[2]).

Experimental

All the solvents employed in the present studies were of analytical grade and were further purified according to the standard procedures. Diphenyl sulphoxide and peroxybenzoic acid were prepared and used, as reported previously.[3] The peroxybenzoic acid was prepared just before use and standardized iodometrically.

Kinetic Measurements.—Solutions (50 ml) each of the sulphoxide and the peroxyacid in the desired solvents were used for kinetic measurements at $30.0° \pm 0.5°$. The temperature was thermostatically controlled and the progress of the oxidation was followed iodometrically at convenient time intervals. In all these experiments the concentration of the sulphoxide was always in excess (about 10 times) of the peroxy acid in all the solvents. The idea of using such a ratio was to change the second order kinetics to the first order. Two to three such measurements were carried out with different concentrations of the sulphoxide in every solvent. The summary of the results is given in Table 2.

Discussion

It is a well-known fact that many a reaction are affected when a change is brought about in the solvent medium. A number of equations have been proposed for the quantitative correlation of the rate of the reaction with the nature of the solvent.[4] However, Hughes and Ingold have forwarded a qualitative theory of solvent effects on reaction kinetics, since none of the quantiative equations afforded a complete generalization.[5] According to Ingold and his colleagues, an increase in the ion-solvating power of the medium will accelerate the creation of and concentration of charges and inhibit their destruction and diffusion. Thus, a more polar solvent will accelerate or retard reaction according as the transition state is more or less polar than the initial state. Although this theory is not entirely general, yet on its basis a number of predictions, regarding the effects of the solvents on the rates of reaction were made that have come true.[6-9]

It has already been mentioned that the present studies were initiated with a view to determining the influence of the solvent on the oxidation rates. A larger variation in the dielectric constant of the

TABLE 1.—DETERMINATION OF THE OVERALL ORDER OF PEROXYBENZOIC ACID OXIDATION OF DIPHENYL SULPHOXIDE (AT $30.0 \pm 0.5°$) BY THE INTEGRATION METHOD.

Time sec	ml of 0.001N Na$_2$S$_2$O$_3$ $(a-x)$	log $(a-x)$	Time sec	ml of 0.001N Na$_2$S$_2$O$_3$ $(a-x)$	log $(a-x)$
	CYCLOHEXANE			ACETONE	
115	7.80	0.8921	300	8.15	0.9112
195	5.40	0.7324	600	7.37	0.8675
280	4.28	0.6314	900	6.68	0.8248
365	3.92	0.5933	1200	6.10	0.7853
465	3.10	0.4914	1500	5.66	0.7528
570	2.68	0.4281	1800	4.95	0.6946
660	2.06	0.3139	2100	4.58	0.6609
720	1.86	0.2695	2400	4.20	0.6232
780	1.64	0.2148			
	BENZENE			ETHANOL	
105	6.60	0.8195	180	8.20	0.9138
195	6.26	0.7966	375	7.46	0.8727
285	5.70	0.7559	630	6.84	0.8351
405	5.20	0.7160	840	6.20	0.7924
660	4.48	0.6513	1035	5.80	0.7634
720	4.30	0.6335	1335	5.58	0.7466
780	4.18	0.6212	1590	5.12	0.7093
840	4.00	0.6021	1830	5.00	0.6990
			2110	4.68	0.6702
	TOLUENE			METHANOL	
60	7.86	0.8954	210	11.90	1.0755
115	7.35	0.8663	390	11.26	1.0515
185	6.98	0.8439	720	10.70	1.0294
240	6.38	0.8048	885	10.30	1.0128
300	5.98	0.7767	1155	10.00	1.0000
360	5.80	0.7634	1260	9.64	0.9841
425	5.40	0.7324	1430	9.50	0.9777
485	5.24	0.7193	1695	9.10	0.9590
	n-PROPANOL			ACETONITRILE	
300	6.18	0.7910	270	15.74	1.1970
465	5.98	0.7767	680	13.10	1.1173
585	5.20	0.7160	965	12.58	1.0997
1085	3.90	0.5911	1245	11.88	1.0748
1230	3.80	0.5798	1500	10.92	1.0342
1435	3.50	0.5441	1985	9.40	0.9731
			2235	8.60	0.9345

Note:- Concentration of diphenyl sulphoxide in benzene and acetone is 2.5 m moles and in all other solvents 5.0 m moles.

solvent medium was sure to effect the rate in the light of what has been stated above. Therefore, the solvents that have been employed in these investigations were directly selected for this reason.

Some of the experimental data employed in the determination of the order of these oxidations is shown in Table 1. First order plots were excellent straight lines and typical representatives are shown in Fig. 1. The slope of such first order plot was calculated using the method of least squares. Second order rate constant was, then, derived
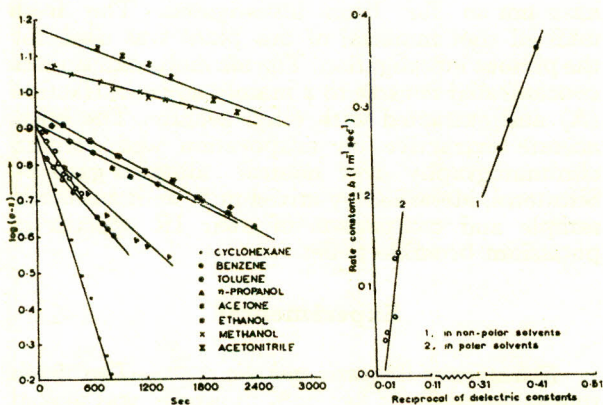
from this slope by employing the equation:

$$2.303 \times \frac{\text{Slope of the first order plot}}{\text{concentration of the sulphoxide in moles}}$$

Specific rate constants obtained in this manner along with the dielectric constants of the solvents are recorded in Table 2. This reveals that with the increase of dielectric constants, hence polarity, there results a decrease in the specific rate constants. This suggests that these oxidations, like the oxidation of sulphides to sulphoxides,[10] do not involve ions in the transition state. The mechanistic path for this oxidation may, thus, be formulated as follows:
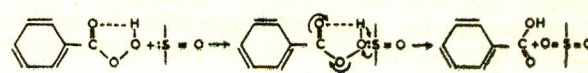
Transition state (i)

The non-ionic peroxy acid in the hydrogen-bonded state (i) facilitates the nucleophilic displacement. However, the probability of the peroxy acid in the cyclic form is more in the non-polar solvents than in the polar solvents.

Fig. 1.—First-order rate plots for peroxybenzoic acid oxidation of diphenyl sulphoxide at 30.0° ± 0.5°.

Fig. 2.—Plots of rate constants vs. reciprocal of dielectric constants.

TABLE 2.

Solvents	Dielectric constants	Concentrations of sulphoxide in mmoles	Rate constants	
			k l.m^{-1} sec^{-1}	Mean k l.m^{-1} sec^{-1}
Cyclohexane	2.05	5.0 2.5	0.35 0.37	0.36 ± 0.01
Benzene	2.283	5.0 2.5	0.281 0.280	0.28 ± 0.001
Toluene	2.379	5.0 2.5	0.245 0.259	0.25 ± 0.005
n-Propanol	20.1	5.0 2.5	0.139 0.134	0.136 ± 0.003
Acetone	20.7	5.0 2.5	0.131 0.129	0.130 ± 0.001
Ethanol	24.3	5.0 2.5 2.5	0.065 0.068 0.064	0.066 ± 0.002
Methanol	32.63	5.0 5.0 2.5	0.048 0.050 0.046	0.048 ± 002.2
Acetonitrile	38.8	5.0 2.5	0.043 0.038	0.040 ± 0.003

A plot of the rate constants, shown in Table 2, versus the reciprocal of the dielectric constants of the solvents is depicted in Fig. 2. It is obvious from this figure that there is a linear relationship between the rate constants and the reciprocal of the dielectric constants of the polar as well as the non-polar series of the solvents respectively. It is, therefore inferred that rate constants are inversely proportional to the dielectric constants of the solvents in both the series.

The empirical findings in our previous work are thus elaborated in the present studies. It is also seen that a change in the dipole moment of each series of the solvents has little effect on the proposed generalization.

References

1. S. A. Khan, M. Ashraf, A. B. Chughtai and I. Ahmad, Pakistan J. Sci. Ind. Research, **10**, 3, 151-154 (1967).

2. A. A. Maryott, and E. A. Smith, *Table of Dielectric Constants of Pure Liquids*, NBC Circular 514, August 10 (1950).

3. M. Ashraf, A. B. Chughtai and S.A. Khan, Scientific Researches (Dacca) **2**, 135-140 (1967).

4. A. A. Frost and R.G. Pearson, *Kinetics and Mechanism* (J. Wiley, Inc., New York, 1961), second edition, p. 123-159.

5. E. D. Hughes and C.K. Ingold, J. Chem. Soc., 244 (1935).

6. C. A. L. de Bruyn and A. Steger, Rec. Trav. Chim., **18,** 41, 311 (1899).

7. E. D. Hughes, J. Chem. Soc., 255 (1935).

8. L. J. LeRoux, S. Sudgen and R.H.K. Thompson, J. Chem. Soc., 586 (1945).

9. W. C. Davies and W.P.G. Lewis, J. Chem. Soc., 1599 (1934).

10. C. G. Overberger and R.W. Cummins, J. Am. Chem. Soc., **75,** 4250 (1953).

ISOLATION OF β-SITOSTEROL FROM CAPPARIS APHYLLA

M. MANZOOR-I-KHUDA* and (Miss) Z. KAPADIA

Drugs, Pharmaceutical and Pesticide Division, Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

The chemical constituents of *Capparis aphylla* have not so far been investigated. The fresh undried root material of this plant was used for the present investigation. The alcoholic extract was concentrated *in vacuo* to a mainly aqueous fraction (A) and extracted with ethyl acetate. The ethyl acetate extractive on evaporation and column chromatography over neutral alumina gave β-Sitosterol, identified by mixed m.p. with authentic sample and comparison of their IR spectra in potassium bromide pellet.

Experimental

Extraction of Capparis aphytla roots.—The fresh root material (3.85 kg; 32% moisture) was soaked in ethanol (7 l.) at room temperature for 3 days. The extraction was repeated with ethanol (6 l.) twice at room temperature over a period of 4 days. The total extracts were concentrated in a cyclone evaporator to approximately 1.5 l. This mainly aqueous layer was extracted with ethyl acetate (*Ca* 300 ml) and the dried (Na_2SO_4) organic layer evaporated to give 28 g of a semi-solid greasy material.

Isolation of β-Sistosterol.—The ethyl acetate extractive (28 g) was leached with benzene to give a benzene-soluble portion (11.5 g), which was then chromatographed on neutral alumina (215 g), the elution being carried out with benzene, 30% and 60% ether in benzene, 25%, 50% and 75% chloroform in ether, chloroform, 1%, 5%, 10%, 15%, 20% and 25% methanol in chloroform. The benzene elute was collected in 18 fractions and the fractions from 11 to 18 were combined to give 11.5 g of a crude crystalline material (m.p. 105–120°C). This was repeatedly crystallised from methanol (10 times), finally giving β-sitosterol, m.p. and mixed m.p. with an authentic sample 136–37°C. The IR spectrum taken in potassium bromide pellet was found to be superimposable on the IR spectra of authentic β-sitosterol.

*Present address: Technological Research Board, Jute Research Institute, Dacca-15.