ACTA CHEMICA SCANDINAVICA 16 (1962) 495–500

An Experimental Approach to the Study of Radical Formation and Recombination Processes

KJ. ROSENGREN*, S. SUNNER and D. TIMM

Thermochemistry Laboratory **, *University of Lund, Lund, Sweden*

An instrumental design is described for the irradiation of light absorbing substances and for the recording of spectra of their decomposition products in a rigid matrix at 77°K, using high pressure mercury lamps and a double-beam recording spectrophotometer. The performance of the assembly has been tested by photolyzing carbon disulfide and ethyl iodide.

The determination of bond energies is one of the principal objects of molecular energetics. For covalent bonds it can be done in one or both of two principally different ways. Either, the direct determination of a specific fragmentation of a molecule may give a value of the *bond dissociation energy* of a particular bond, or, from thermochemical heat of combustion or heat of reaction measurements a value of the *thermochemical bond energy term* may be derived [1].

It should be of considerable theoretical value to devise a method for the direct measurement of *bond formation energies* by studying calorimetrically the radical recombination reaction

$2\,\mathrm{A}\times \rightarrow \mathrm{A}_2$***

Such a method was used by Bichowsky and Copeland [2,3(p. 26)] in determining the heat of formation of H_2 from hydrogen atoms. These were obtained by flowing H_2 through an electric discharge. From measurements of the change in pressure and of the heat release at a platinum surface, the recombination energy was obtained. Obviously, this method is limited to a few cases with very small molecules, where the dissociation process can be unambiguously established.

---

* Research Fellow at *The Swedish Technical Research Council.*

** Sponsored by *The Swedish Natural Science Research Council* and *The Swedish Technical Research Council.*

*** For obvious reasons, this experiment can be performed unambiguously only if the two radicals are identical. In the case of ionic species or formation of bonds of an electron donor-acceptor type the species must of course be different.

To achieve a more general applicability it was deemed necessary to turn to the study of prodution and behaviour of radicals in a condensed state. The problems coped with are here connected with the fulfilment of the following conditions:

1. One — and only one — radical species must be generated in an otherwise non-reactive system.
2. The nature and the amount of the radical must be established. During the procedure the system must be reasonably stable.
3. The recombination reaction must be clean.
4. Further, it must be initiated and completed within the boundaries of a calorimetric system.

Although it was realized that it should be a formidable task to find ways and means by which these conditions could be fulfilled and that the ultimate goal certainly was quite afar, it was felt that results which might be gained could easily justify a careful exploration of the possibilities inherent in this experimental approach.

EXPERIMENTAL APPROACH

The first condition given above was judged to be the most crucial. Although in recent years a very pronounced interest has been shown in the study of free radicals and a considerable amount of information has been gained [4,5], still very little is known about stoichiometric relations in radical formation processes. This being so, the assumption was made that, provided means could be found to split homolytically a symmetrical molecule into two identical radicals, the chemistry of the overall process should be very much simplified. Among a number of possible classes of substances symmetrical aliphatic disulfides were chosen for several reasons. This particular aspect will be elaborated in a later paper [6].

The third condition put severe restrictions on both methods for formation as well as for determination of concentration of reactant and reaction product(s). The calorimetric procedure required the size of the sample container to be at least a few milliliters and its shape to approach spherical symmetry. Thus, some of the most common techniques for radical formation as well as trapping were out of the question. It was therefore decided to start out by exploring the method used by Lewis and Lipkin [7], Norman and Porter [8] and others, namely, to photolyze a compound at liquid nitrogen temperature in a rigid matrix consisting of a mixture of organic solvents and — as a possible analytical tool — to study the spectral changes in the UV and visible regions.

Thus, it was required to design and build a unit for photolysis as well as a compartment for work at liquid nitrogen temperature accomodating an appropriately designed sample cell and an identical reference cell to be used in connection with a recording double-beam spectrophotometer. The construction of the cell compartment has been given in the preceding paper [9]. The present paper gives a description of the photolysis equipment and reports the results of some test experiments.

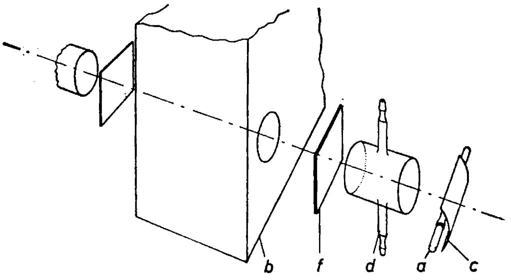

Fig. 1. Lay-out of photolysis equipment.

Apparatus

Photolysis equipment. High pressure mercury lamps, *a*, Philips SP 900 W, were mounted on each side of the cell compartment, *b*, within surface-aluminized parabolic reflectors, *c*, and equipped with appropriate cooling devices and filters (Fig. 1). The filter consisted of 3. 5 cm of a nickel sulphate solution [10] (285 g of $NiSO_4$, 6 H_2O per liter of solution) which was pumped through a cell, *d*, (o.d. 35 mm, cell length 35 mm) and cooled by tap water in a spiral condenser *. The total amount of irradiation has been measured with a uranyl oxalate actinometer and corresponds to 1.8×10^{17} quanta per second and cm^2. Besides, glass filters, *f*, could be inserted into the light beam.

Cells and cell compartment. In the standard procedure cylindrical quartz cells, o.d. 22 mm and i.d. *ca.* 19 mm, cell length 17 mm, were used. The sealed-on, optically polished windows were made of Ultrasil, wall thickness 1.5 mm. The 9 mm inner diameter stem had a quartz to Pyrex graded seal. The cell compartment has been described in a preceding paper [9].

Spectrophotometer. A Unicam model SP 700 double-beam recording spectrophotometer was used, the only change being made was the replacement of the standard cell compartment with the low temperature unit [9]. The recording was made linearly in wave-numbers and, hitherto, with direct reading in percent transmission. The spectrophotometer was calibrated using Philips spectral lamps type 93 106 E (Zn) and type 93 109 E (Hg, low pressure).

Materials

Glass-forming hydrocarbons. Different mixtures of isopentane with 3-methyl pentane were used as glass-forming liquids (6:1 and 2:3 by volume, Ref.[11] and Ref.[8], respectively). In addition, a new mixture of hydrocarbons was tried, *viz.* pentane and *neo*-hexane (3:8 by volume) [12]. The purification and purity determination of the substances will be described elsewhere [13].

Carbon disulfide was purified according to Vogel [14]. From gas-chromatographic studies, the purity was judged to be better than 99.95 %.

Ethyl iodide was purified by fractional distillation. Estimated purity (gaschromatography) better than 99.95 %.

Experimental procedure

Filling of the cells. The stem of the quartz cell was sealed to a shirted standard joint cone by which connection could be established with a high vacuum line. The cells were pumped until the pressure dropped beyond 10^{-4} mm Hg and thereupon they were filled with dry air.

---

* Metal parts were carefully avoided, the pump being made of lucite. The light transmission of the solution was unaffected after 30 h of operation.

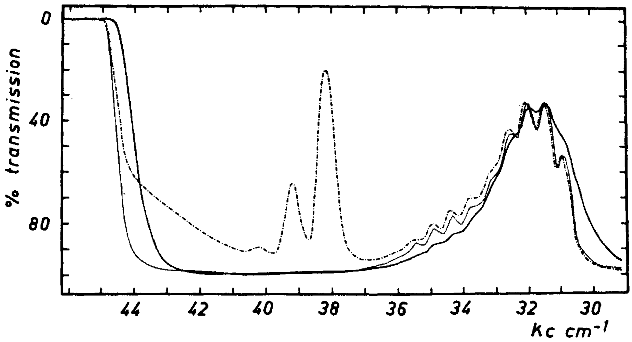

Fig. 2. Spectra of 5 mM solution of carbon disulfide in isopentane/3-methyl pentane (6:1). ——— 298°K; ····· 77°K; —·—·— 77°K after 5 min of photolysis.

All solutions were prepared under careful exclusion of moisture and transferred to the cells through an adapter using a slight overpressure of dry air and under perfectly anhydrous conditions. The amount of solution was so chosen that, after the contraction was completed during cooling, the meniscus was found in the lowest part of the stem. Each cell was then connected to the vacuum-line and the solution was degassed by gentle boiling at room temperature. It was then frozen down to liquid nitrogen temperature, full vacuum was applied, and the cell was sealed off.

Both the sample cell and the reference cell containing pure solvent mixture were inserted into the cell compartment and a spectrum was recorded. Liquid nitrogen of 99.8 % purity (Philips liquifier PW 7 050) was then blown from the storage tank through a vacuum-mantled 250 × 14 mm glass tube packed with quartz-wool (diam. 0.004 – 0.012 mm) into the cell compartment. The quartz-wool removed even traces of solid impurities from the refrigerant. The duration of the filling operation was *ca.* 30 min whereupon the system was allowed to stand for 10 min to reach thermal equilibrium.

From the start of the filling operation the outer windows of the evacuated quartz cylinders in the cell compartment were electrically heated, a total of *ca.* 20 W being sufficient to prevent condensation.

A spectrum was recorded at 77°K and the cell compartment was brought to the photolysis set-up. The sample was irradiated for a certain time and then reinserted into the spectrophotometer where the spectrum of the irradiated sample was taken. The procedure with intermittent irradiation and spectrum recording could be repeated until the liquid nitrogen level interfered with the light beam, the total possible time of work at 77°K being about 3.5 h before it became necessary to refill with nitrogen.

Spectrophotometer accuracy. Twice a week both cells were filled with pure solvent mixtures and the 100 % line of the spectrophotometer was adjusted using the built-in multipot system. The reproducibility between consecutive control experiments was usually better than 1 % in the hydrogen lamp region and 2 % in the tungsten lamp region. A separate experiment with solvent-filled cells showed that, when liquid nitrogen was introduced into the cell compartment, the curvature produced in the 100 % line was less than ± 2 % in the region 50 – 13 kc cm^{-1}.

Before a spectrum was recorded the 0 and 100 % lines were adjusted at a wave number where a preliminary experiment had shown no absorption to occur during the experiment. Although the spectrophotometer is equipped with a continuous strip chart recorder, the paper could be rewound and several spectra recorded on the same paper, the reproducibility being better than 10 cm^{-1}.

TESTING OF THE EQUIPMENT

Carbon disulfide. Photolysis of CS_2 in rigid solvents at 77°K has been studied by Norman and Porter[8] and their experiments have been reproduced by Sowden and Davidson[15]. We have photolyzed CS_2 in an isopentane/3-methyl pentane (6:1) glass using 0.2 and 5 mM solutions.

Fig. 2 shows the spectral changes during photolysis, the result from the more concentrated solution being similar to those already published. However, an increased absorption between 32 and 37 kc cm^{-1} indicates the formation of S_2. Upon longer irradiation of the concentrated sample, it becomes turbid (probably caused by aggregates of sulfur atoms) and the light transmission shows a steady decrease starting in the visible and becoming more pronounced throughout the UV region. After a total time of irradiation of 90 min, the sample had a pale yellow colour which persisted on warming up to room temperature.

Accurate measurements of the wave-numbers at the two largest CS peaks give the result 38.16 and 39.20 kc cm^{-1} in agreement with 38.15 and 39.17 kc cm^{-1}, respectively, reported in Ref.[8] Besides these known CS spectral peaks, the more diluted solution upon longer photolysis also showed a decidedly reduced transmission between 45 and 40 kc cm^{-1}.

Ethyl iodide. Photolysis of ethyl iodide has been studied by Norman and Porter[8]. We repeated these experiments in the three hydrocarbon mixtures mentioned above, in concentrations between 0.1 and 1.0 mM, most experiments being performed in a 0.25 mM solution.

In the isopentane/3-methyl pentane (2:3) glass, the only change of the recorded spectrum upon irradiation for 60 min was a marked decrease of the EtI absorption band at 39.2 kc cm^{-1}. However, upon warming the glass above its softening point, the spectrum changed radically and three new absorption bands appeared at 34.6, 25.7 and 21.3 kc cm^{-1}, associated with the formation of molecular iodine, I_2. At the same time the colourless glass became yellow. When EtI was photolyzed, either in the isopentane/3-methyl pentane (6:1) glass or in the pentane/*neo*-hexane (3:8) glass, the same spectral changes occurred even at liquid nitrogen temperature, indicating less rigidity of these matrices[13].

These results — as far as the change in spectrum is concerned — are in agreement with those reported in Ref.[8]

Acknowledgement. This investigation has been supported by *Directorate of Chemical Science, AFOSR, AFRD of the Air Research and Development Command, United States Air Force,* through its European Office, by the *Swedish Technical Research Council* and by *Knut and Alice Wallenbergs Stiftelse.*

REFERENCES

1. Cottrell, T.L. *The Strengths of Chemical Bonds.* 2nd Ed. Butterworths Scientific Publications, London 1958.
2. Bichowsky, F. R. and Copeland, L. C. *J. Am. Chem. Soc.* **50** (1928) 1315.
3. Szwarc, M. *Quart. Rev.* **5** (1951) 22.
4. Bass, A. M. and Broida, H. P. *Formation and Trapping of Free Radicals.* Academic Press, New York and London 1960.

5. Minkoff, G. J. *Frozen Free Radicals.* Interscience Publishers Inc., New York 1960.
6. Rosengren, Kj. *Acta Chem. Scand.* **16** (1962) *In press.*
7. Lewis, G. N. and Lipkin, D. *J. Am. Chem. Soc.* **64** (1942) 2801.
8. Norman, I. and Porter, G. *Proc. Roy. Soc. London* **A230** (1955) 399.
9. Rosengren, Kj., Sunner, S. and Timm, D. *Acta Chem. Scand.* **16** (1962) 467.
10. Kasha, M. *J. Opt. Soc. Amer.* **38** (1948) 929.
11. Potts, W. J. *J. Chem. Phys.* **21** (1953) 191.
12. Rosengren, Kj. and Sunner, S. *Acta Chem. Scand.* **16** (1962) 521.
13. Rosengren, Kj. *Acta Chem. Scand.* **16** (1962) *In press.*
14. Vogel, A. I. *A Text-book of Practical Organic Chemistry.* 3rd Ed. Longmans, Green and Co., London 1956.
15. Sowden, R. G. and Davidson, N. *J. Am. Chem. Soc.* **78** (1956) 1291.

Received September 30, 1961.