~~Final Report~~ upper case

(6) Infrared Studies of Free Radicals and Unstable Reaction Intermediates.

at the

University of California
Berkeley, California

~~Principal Investigator:~~ (10) by George C. Pimentel
~~Professor of Chemistry~~

(9) Final rept. 1 Jul 56 - 28 Feb 61,

(15) Contract ~~No.~~ AF 49(638)-1
Division File No. Chem. 10-8

~~1 July, 1956 - 28 February, 1961~~

438297

Submitted
August 15, 1961
Department of Chemistry
University of California
Berkeley 4, California

Director of Chemical Sciences (SRQ)
Air Force Office of Scientific Research (ARDC)
Washington 25, D.C.

I. Research Program

All of the research problems studied exploited the matrix isolation method as developed at the University of California laboratories. In this method, substances are suspended in solid nitrogen or an inert gas and then studied spectroscopically. The Berkeley laboratory developed this technique with emphasis on the infrared spectral region.

At the time of the initiation of this Air Force support, the matrix isolation technique was practically new. The development of the unique potentialities of the method was significantly aided and accelerated by this financial aid. The work has been fruitful and a new research method has been demonstrated for the detection and study of transient species. Of course, the current importance of the spectroscopic study of high temperature reactions makes this work timely and useful.

Specific novel applications of the method are listed.

First Infrared Detection of Reactive Species

The detection of HCO is the first definite infrared identification of any triatomic free radical, except for NO_2, by any technique.

Formyl radical, HCO	:	definite (see publication No. 6).
Nitroxyl, HNO	:	definite (see publication No. 13).
NH_2 or N_2H_2	:	identification still doubtful (see publications No. 10, 17).
CH_2	:	identification still doubtful (see publications No. 5, 12).

iso-diazomethane : identification still doubtful (see publications No. 5, 12).

N_3 : identification still doubtful (see publication No. 19).

Chemistry of Reactive Species

The matrix method gives a unique opportunity to study the reactions of free radicals under conditions where secondary reactions are interrupted.

Hydrogen abstraction by CH_3 : (see publication No. 2)

Reaction of NH with O_2 : (see publications No. 3, 15)

Isomerization of nitrous acid: (see publication No. 3)

Chemiluminescence of C_2H_4 formed from CH_2 : (see publication No. 4).

Primary Act of Photolysis

Because of the inert environment, the primary act of photolysis can be learned in the condensed phases. This is always the crucial reaction in the elucidation of photolysis.

Methyl iodide and the cage effect: (see publication No. 2)

Nitromethane : (see publications No. 11, 13)

Methyl nitrite : (see publication No. 13).

Hydrogen Bonding

Narrowing of bands of hydrogen bonded polymers gives this method power to segregate the infrared spectra of polymers of different size. No other method permits this.

Water : (see publication No. 16)

Methanol : (see publication No. 18)

Hydrazoic acid : (see publication No. 10).

Formyl Radical, HCO

The detection of HCO by infrared methods has an historic significance. Because of the low absorption coefficients in the infrared, ~~the~~ only two or three diatomic free radicals had been detected earlier (in flames). These were detected mainly because electronic spectroscopy made possible accurate predictions of the absorption frequencies. Diligent search in this laboratory and others for evidence of NH_2 in flames was indecisive. The matrix isolation method was developed in this laboratory to meet the need for a new approach.

Formyl was produced by photolyzing hydrogen iodide, HI, in solid CO. The identification was verified by detection of both infrared and visible absorption of HCO (see publication No. 6).

Diazomethane, CH_2N_2: A search for CH_2

On photolysis, diazomethane decomposes to form CH_2 and the stable N_2 molecule. It seems to offer a unique opportunity to form CH_2 under conditions that will permit storage and leisurely spectroscopic study of this interesting molecule. Diazomethane was suspended in N_2 and in Ar and photolyzed *in situ* at 20°K. The products were shown to be distinguishable from the stable products obtained from photolysis of the pure material, either gas or solid. Infrared and visible ultraviolet spectra features were detected which could be assigned to unidentified, presumably unusual molecular species. A thermoluminescent behavior was observed for the first time. Species which could contribute to the spectra include methylene, CH_2, and an isomeric form of diazomethane. The thermoluminescence was assigned to excited C_2H_4 formed on diffusion (see publications, No. 4, 5, and 12).

Nitroxyl, HNO

Both nitromethane and methyl nitrite were photolyzed in solid argon at 20°K. For the first time, methyl nitrite was identified as a photolysis product of nitromethane, both in the matrix and in the gas. Nitroxyl, HNO, was detected in the infrared and identified for the first time (see publications, Nos. 11 and 13).

Hydrazoic acid, HN_3

Photolysis of HN_3 is expected to produce NH, yet it has never been observed directly. In solid nitrogen, absorptions develop but they are surely not caused by NH. Evidence is considerable that the photolysis produces either NH_2 or N_2H_2, though which is not yet clear. Neither species has been definitely identified in the infrared region (see publications, Nos. 10 and 17).

In addition, these experiments and others led to a tentative infrared identification of N_3. Subsequent work has not provided confirmation of the assignment, though it is generally postulated that a nitrogen atom suspended in solid nitrogen forms some sort of a complex $N \cdot N_2$ (see publication, No. 19).

Nitrous Acid, HONO

The photolysis of hydrazoic acid, HN_3, in solid nitrogen containing a small amount of oxygen, produces nitrous acid, HONO, in both _cis_ and _trans_ forms. This was the first report of this reaction of the radical NH.

$$NH + O_2 = HONO$$

It was discovered that near infrared irradiation of the argon suspension of HONO results in a conversion of _cis_-HONO into _trans_-HONO. The reaction can be reversed by ultraviolet irradiation. This was the first report of an infrared-induced isomerization. This novel reaction is still under study (see publications, Nos. 3 and 15).

Hydrogen abstraction by methyl radicals

The photolysis of CH_3I in solid nitrogen provides a source of methyl radicals with known energy and controlled environment. Various substances have been included in the matrix and quantitative study of the reactions that occur has been carried out. The chemistry of the methyl radicals shows that they react as do methyl radicals at 2000°K. The effect of the matrix cage is examined (see publications, No. 2).

II. Personnel

In addition to two faculty personnel, the project has involved the research activities of two post-doctoral students, nine graduate students, and one undergraduate student. The thesis titles of the graduate students who participated are listed.

Faculty personnel

Dr. George C. Pimentel, Professor

Dr. Bruce H. Mahan, Associate Professor

Post-doctoral personnel

Dr. Sydney Leach

Dr. Warren Thompson

Graduate student personnel and present occupation

John D. Baldeschwieler, Instructor, Harvard University.

C. David Bass, Atomics International, Canoga Park, Calif.

George E. Ewing, Jet Propulsion Laboratory, Pasadena, Calif.

Harmon W. Brown, Varian Instruments Co., Palo Alto, Calif.

Theodore D. Goldfarb, Assistant Professor, New York State University, Oyster Bay, New York.

Ivan Haller, IBM, Poughkeepsie, New York.

James Hanlan, graduate study not completed.

Dolphus E. Milligan, Research Scientist, Mellon Institute, Pittsburth, Pa.

Mathias Van Thiel, University of California, Radiation Laboratory, Livermore, Calif.

Undergraduate student personnel

Gerry Rollefson

Thesis titles

John D. Baldeschwieler (1959) "The Structures of Unstable Compounds by Matrix Isolation Techniques."

C. David Bass (1961) "Photolytic Processes in Solids."

Harmon W. Brown (1958) "A Study of Photolysis at Extremely Low Temperatures."

George E. Ewing (1961) "Spectroscopic Studies of Substances at Low Temperatures."

Theodore D. Goldfarb (1959) "Spectroscopic Studies of Diazomethane and its Unstable Photolytic Products."

Ivan Haller (1961) "Matrix Isolation Studies Using Far Ultraviolet Photolysis and the Structure of Some Unstable Molecules."

Dolphus E. Milligan (1958) "Spectroscopic Studies of Reaction Intermediates at Extremely Low Temperatures."

Mathias Van Thiel (1957) "Matrix Isolation Studies of Reactive Molecules."

Publications: 1956-1961

1961		AFOSR TN Number	Date
✓1.	"The Infrared Spectrum of Solid Carbon Monoxide," by G. E. Ewing and G. C. Pimentel, J. Chem. Phys. (in press)	~~DL~~ 242 AD 254304	1 Feb. 1961
✓2.	"Hydrogen Abstraction from Hydrocarbonds by Methyl Radicals from the Photolysis of Methyl Iodide in Solid Nitrogen," by C. D. Bass and G. C. Pimentel, J. Am. Chem. Soc. (in press). JACS 83: 3754-3758: Sep 1961	~~Not yet assigned~~ AFOSR 1067 AD 274797	31 Mar. 1961

1960			
✓3.	"Light-Induced cis-trans Isomerization of Nitrous Acid Formed by Photolysis of Hydrazoic Acid and Oxygen in Solid Nitrogen," by J. D. Baldeschwieler and G. C. Pimentel, J. Chem. Phys. 33, 1008-1015 (1960).	AFOSR TN-60-1018 AD 246358	31 Aug. 1960
✓4.	"The Chemiluminescence of Ethylene Formed Probably from Methylene in an Inert Matrix," by T. D. Goldfarb and G. C. Pimentel, J. Chem. Phys. 33, 105-108 (1960).	AFOSR TN-60-182 AD 233368	10 Feb. 1960
✓5.	"Spectroscopic Study of the Photolysis of Diazomethane in Solid Nitrogen," by T. D. Goldfarb and G. C. Pimentel, J. Am. Chem. Soc. 82, 1865-1868 (1960).	AFOSR TN-59-991 AD 227605	25 Sept. 1959
✓6.	"Infrared Detection of the Formyl Radical, HCO," by G. E. Ewing, W. E. Thompson, and G. C. Pimentel, J. Chem. Phys. 32, 927-932 (1960); see also Erratum, J. Chem. Phys. 34, 1067 (1961).	AFOSR TN-59-1197 AD 228570	1 Nov. 1959
✓7.	"The Photolysis of Carbon Monoxide," by B. H. Mahan, J. Chem. Phys. 33, 959-965 (1960).	AFOSR TN-60-472 AD 237420	9 May 1960
✓8.	"The Perturbation of Molecular Distribution Functions by Chemical Reaction," by B. H. Mahan, J. Chem. Phys. 32, 362 (1960).	AFOSR TN-59-990 AD 227606	21 Sept. 1959

		AFOSR TN Number	Date
9.	Chapter IV: Radical Formation and Trapping in the Solid Phase, by G. C. Pimentel in "Formation and Trapping of Free Radicals," Edited by H. Broida and A. M. Bass, Academic Press, Inc., New York (1959).	None	--
10.	"Matrix Isolation Studies, Infrared Spectra of Intermediate Species in the Photolysis of Hydrazoic Acid, II," by M. Van Thiel and G. C. Pimentel, J. Chem. Phys. 32, 133-140 (1960).	AFOSR TN-59-223 AD211805	25 Feb. 1959
1959			
11.	"Formation of Methyl Nitrite in the Photolysis of Gaseous Nitromethane," by G. C. Pimentel and G. Rollefson.	AFOSR TN-59-268 AD 212469	28 Feb. 1959
1958			
12.	"Matrix Isolation Studies: Possible Infrared Spectra of Isomeric Forms of Diazomethane and of Methylene, CH_2," by D. E. Milligan and G. C. Pimentel, J. Chem. Phys. 29, 1405-1412 (1958).	AFOSR TN-58-818 AD202 643	10 Sept. 1958
13.	"Photolysis of Nitromethane and of Methyl Nitrite in an Argon Matrix; Infrared Detection of Nitroxyl, HNO," by H. W. Brown and G. C. Pimentel, J. Chem. Phys. 29, 883-888 (1958).	AFOSR TN-58-429 AD 158232	10 May 1958
14.	"The Promise and Problems of the Matrix Isolation Method for Spectroscopic Studies," by G. C. Pimentel, Spectrochimica Acta 12, 94-96 (1958).	~~None~~ AFOSR 4308	--
15.	"Reaction Kinetics by the Matrix Isolation Method: Diffusion in Argon; cis-trans Isomerization of Nitrous Acid," by G. C. Pimentel, J. Am. Chem. Soc. 80, 62-64 (1958).	AFOSR TN-57-328 II AD 132401(b)	15 June 1957

1957		TN Number	Date
16.	"Infrared Studies of Hydrogen Bonding of Water by the Matrix Isolation Technique," by M. Van Thiel, E. D. Becker, and G. C. Pimentel, J. Chem. Phys. 27, 486-90 (1957).	57-328 I AD 132401(a)	15 June 1957
17.	"Matrix Isolation Studies: Infrared Spectra of Intermediate Species in the Photolysis of Hydrazoic Acid," by E. D. Becker, G. C. Pimentel, and M. Van Thiel, J. Chem. Phys. 26, 145-50 (1957).		
18.	"Infrared Studies of Hydrogen Bonding of Methanol by the Matrix Isolation Techniques," by M. Van Thiel, E. D. Becker, and G. C. Pimentel, J. Chem. Phys. 27, 95-99 (1957).		
19.	"Infrared Absorption by the N_3 Radical," by D. E. Milligan, H. W. Brown, and G. C. Pimentel, J. Chem. Phys. 25, 1080 (1956).		