

Preconcentration and Determination of Trace Hexavalent Chromium[Cr(VI)] in Water Samples by Precipitate Flotation

Young-Sang Kim*, Seok-Joon Park, and Jong-Moon Choi

Department of Chemistry, Korea University, Choongnam 339-700

Received August 17, 1992

The separative preconcentration of trace Cr(VI) in a water sample was studied by a precipitate flotation technique. After Cr(III), Al, Mg, and organic materials were removed by the pre-flotation with $\text{Fe}(\text{OH})_3$, trace Cr(VI) in 1.0 L of water sample was coprecipitated by the precipitation of AgCl in the solution of pH 8-9 adjusted with NaHCO_3 . All precipitates were floated by adding mixed surfactants, 1:1 solution of 0.5% sodium oleate and 0.5% sodium dodecyl sulfate ethanolic solutions, and bubbling nitrogen gas. The floats were quantitatively collected on a micropore glass filter by suction and dissolved with conc. ammonia solution. The solution was marked to 25.00 mL with distilled water. Cr(VI) was determined by graphite furnace atomic absorption spectrophotometry. The results for seven determinations of one sample showed relatively good reproducibility with relative standard deviation of 9.71%. Recoveries were 86.0 and 91.0% for sample solutions in which 0.5 and 1.0 ng/mL Cr(VI) were spiked, respectively. The detection limit was improved about 20 times by this method.

Introduction

In contrast to trivalent chromium[Cr(III)], hexavalent chromium[Cr(VI)] is very detrimental in human lung, liver, and kidney by forming complexes with protein or nucleic acid. Therefore, even with trace Cr(VI) existed in various kinds of water such as portable waters, natural waters, and so on, some serious troubles would be induced in human body, animals, and plants. In this sense, it is important to accumulate the informations about the presence of Cr(VI) in water and also it is necessary to develop an accurate analytical method for trace amount of Cr(VI). Recently, it draws an interest in studies on the analytical method and characterization of trace Cr(VI) as well as its environmental effects.

In general, Cr(VI) is on the level of ppb or less in non-contaminated natural waters. Even though detection limits of common analytical instruments such as AAS or AES were much improved, it is still so difficult to determine it directly that the accuracy and precision of analytical results are not favorable. On the other hand, trace elements can sometimes not be determined under the presence of interfering materials. In this case, it is necessary to perform the separation and concentration of analyte elements prior to their determination. Various techniques such as coprecipitation¹, adsorption², ion-exchange³, and solvent extraction⁴ have been widely used for the separation-concentration of trace constituents. These methods are somewhat time-consuming and not so effective to concentrate for a large volume of sample.

In this work, the precipitate flotation technique was applied to determine the trace Cr(VI) in an aqueous solution. This technique is a concentration method by which trace elements are coprecipitated with inorganic or organic precipitate. In order to achieve an efficient concentration, a proper surfactant and gas bubbling are needed to float the precipitates. $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, $\text{Bi}(\text{OH})_3$, $\text{Ti}(\text{OH})_4$, $\text{Zr}(\text{OH})_4$, PbS, and so forth have been commonly used as a coprecipitant⁵⁻¹⁰. Various kinds of organic precipitates have also been used¹¹⁻¹³.

But only a few articles have been reported about the determination of Cr(VI) by the flotation technique. Aoyama and

Hobo¹⁴ floated it as an ion-pair of CrO_4^{2-} with a cationic surfactant, cetyltrimethylammonium bromide. They also made the complex ion of chromium-diphenyl carbazone to be floated by the addition of sodium dodecyl sulfate¹⁵. Such a method is called as an ion-flotation method, but the flotation efficiency was not so high.

Any other studies on the flotation of Cr(VI) by the coprecipitation method could not be found so far. In this work, CrO_4^{2-} was coprecipitated with AgCl as Ag_2CrO_4 in alkaline solution and floated with a mixed surfactant. Conditions of coprecipitation and flotation such as pH of solution, the mole ratio of Ag^+ to Cl^- , the type and quantity of the surfactant added, and so on were optimized, and also interferences and their elimination of coexisted ions were investigated. An optimum procedure was deduced for the determination of trace Cr(VI) in real water samples.

Experimental Section

Reagents and Instruments. All reagents used in this work were of analytical-reagent grade except for NaHCO_3 , sodium oleate and sodium dodecyl sulfate. Aqueous solutions were prepared with distilled and Millipore filtered water.

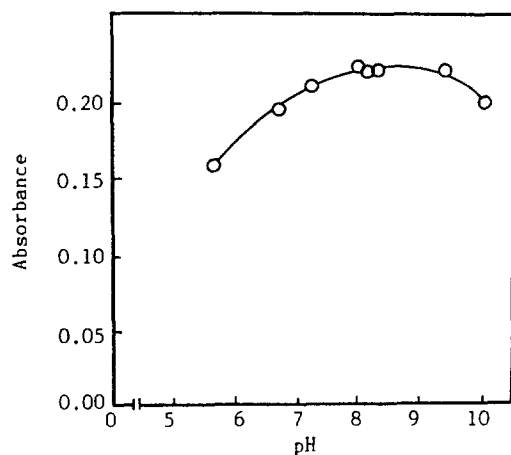
The stock solution of 1.000 $\mu\text{g/mL}$ Cr(VI) was prepared from K_2CrO_4 and used to make standard solutions of proper concentration. Ag^+ solution of 1.0 M was prepared in a brown glass bottle by dissolving AgNO_3 . NaHCO_3 solution of 10% (w/v) was used as a buffer. Ethanolic solutions of sodium oleate (0.5%) and sodium dodecyl sulfate (0.5%) were used as surfactants.

The Perkin-Elmer model 2380 Atomic Absorption Spectrophotometer was employed, which was equipped with model HGA 400 Electrothermal Atomizer. The operating conditions were as follows: wavelength Cr 357.3 nm, lamp current 25 mA, and spectral bandwidth 0.7 nm. The heating program of the graphite furnace was listed in Table 1. The concentrated solution of 20 μL was injected into the graphite tube.

Procedure. Water sample 1 L, from which floating materials were filtered out, was transferred into Erlenmeyer flask. In order to prevent interferences from Cr(III), Al and

Table 1. Furnace Program for Chromium(VI) Determination

Mode	Step	Temperature(°C)	Ramp time(s)	Hold time(s)
Dry	1	90	60	20
Char	2	1200	20	10
Atomize	3	2700	7	3
Clean	4	2800	5	3

**Figure 1.** The effect of pH on the coprecipitation of Cr(VI) with AgCl. [Cr(VI)]: 1.0 ng/mL.

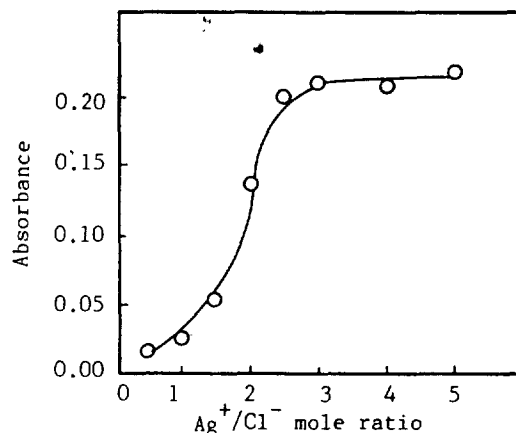
Mg, and organic materials, 4 mL of 0.1 M Fe^{3+} solution was added to the sample and the pH was adjusted to 7-8 with 0.1 M NaOH solution. After stirred for 60 minutes and stood for 3 hours, the mixed surfactant was added and nitrogen gas was bubbled to float out the precipitates in a flotation cell.

The pH of the remaining solution was adjusted to 8.2 with 10% NaHCO_3 solution. After 1 mL of 1.0 M NaCl solution was added, 3 mL of 1.0 M AgNO_3 solution was added to form AgCl coprecipitated with Ag_2CrO_4 . The solution was stirred with a magnetic stirrer for more than 5 minutes. A mixed surfactant (0.5% sodium oleate + 0.5% sodium dodecyl sulfate) solution 1 mL was added to make the precipitates hydrophobic. Nitrogen gas was bubbled at the flow rate of 30-50 mL/min through a fritted glass disc. The floated precipitates were collected in a suction flask and transferred into a glass filter to filter out the solvent. After washed with a small volume of diluted nitric acid, precipitates were dissolved and filtered into a 25 mL volumetric flask with the concentrated ammonia solution. The amount of Cr(VI) was determined with the graphite furnace atomic absorption spectrophotometer (Perkin-Elmer 2380 AAS, HGA-4 Graphite Furnace).

Results and Discussion

Optimum conditions on the coprecipitation and flotation

Effect of pH. Since the chemical species of Cr(VI) varies with the pH of a solution, the efficiency of the coprecipitation and flotation is significantly dependent upon the pH. Jong and Brinckman¹⁶ and Oldham¹⁷ reported that the trace

**Figure 2.** The effect of mole ratio of Ag^+ to Cl^- on the coprecipitation-flotation of Cr(VI). [Cr(VI)]: 1.0 ng/mL.

amount of Cr(VI) was presented as a form of CrO_4^{2-} in a basic solution. In this experiment, Cr(VI) reacts with Ag^+ ion of the first electrical layer to be coprecipitated on AgCl as Ag_2CrO_4 , so that the form of Cr(VI) should be CrO_4^{2-} . To confirm such a fact, the efficiency was investigated under varying the pH of the solution. That is, the absorbance of chromium in the separated and concentrated solution was measured as a function of pH which was changed by adding 10% NaHCO_3 solution into 1.0 $\mu\text{g/L}$ Cr(VI) solution (see Figure 1).

As shown in Figure 1, Cr(VI) was most effectively coprecipitated and floated in the range of pH 8-9. In the basic solution of higher than pH 9, AgOH precipitate was formed so that it seemed to interfere the coprecipitation of Ag_2CrO_4 on AgCl. Such a fact could be confirmed by the formation of faint red precipitates.

On the other hand, NH_4OH and NaOH solutions could not be used to adjust the pH of the sample solution, because NH_4OH formed the ammine complex of Ag(I) which dissolved AgCl precipitate and NaOH did not have any buffer action. Therefore, the solution was adjusted to pH 8.2 with NaHCO_3 solution.

Mole ratio of Ag^+ to Cl^- . Coprecipitation of CrO_4^{2-} on AgCl precipitate was investigated upon the quantity of Ag^+ added. After NaCl solution was added into 1 L of 1.0 $\mu\text{g/L}$ Cr(VI) solution to make 1.0 mM Cl^- , the absorbance of Cr concentrated was measured while the moles of precipitant Ag^+ was varied up to five times of the mole of Cl^- . The absorbance was plotted against mole ratio of Ag^+ to Cl^- (see Figure 2). From the figure, it was known that Cr(VI) was efficiently coprecipitated with AgCl precipitates over 3 mole ratio of Ag^+ to Cl^- . This seems to be caused by the electrostatic attraction of CrO_4^{2-} on the positive surface of AgCl particles having excess Ag^+ . To accomplish the complete coprecipitation, the solution should be stirred with a magnetic stirrer at least for 5 minutes.

Surfactants. The surfactant has been known to play an important role in the flotation of precipitates by forming stable foam layers on the surface of precipitates. Unlike other hydrophobic metal hydroxide, AgCl precipitate which was used as a coprecipitant had some hydrophobic properties, but it was not floated easily without any surfactant because

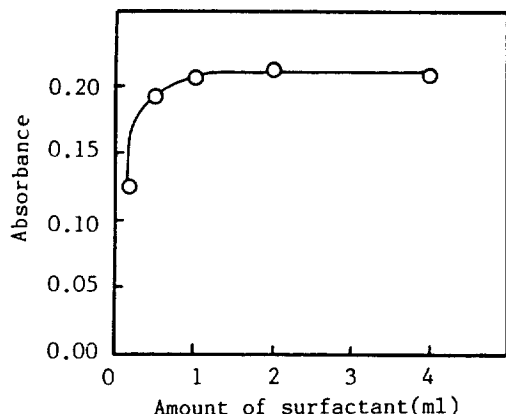


Figure 3. The effect of the amount of mixed surfactant on the flotation. [Cr(VI)]: 1.0 ng/mL.

the precipitate was composed of relatively heavy elements. Therefore, some kind of surfactant was necessary to float the precipitate. Several cationic and anionic surfactants were tested to get the better efficiency of flotation in this experiment. Cationic surfactants such as benzalkonium chloride were not efficient, but anions such as sodium dodecyl sulfate and sodium oleate floated precipitates effectively. These were due to the positive charge on the surface of $\text{AgCl-Ag}_2\text{CrO}_4$ precipitate which was formed by the adsorption of excess Ag^+ ions.

It was confirmed in this work that sodium dodecyl sulfate and sodium oleate were known to show better flotation efficiency than other anionic surfactants. Because sodium oleate had a long chain structure, it could form more stable and tiny foam layers than sodium dodecyl sulfate. Otherwise, sodium dodecyl sulfate had a property to float precipitates promptly. Therefore, the mixture of these two surfactants was used. Nakashima and Yagi⁹, Feng, *et al.*¹⁸ showed excellent results in the flotation of various elements by using this mixed surfactant. The 1:1 mixed solution of each 0.5% surfactant in ethanol was used in this experiment. The ethanol was known to make so fine bubbles of foams that it increased the flotation efficiency of precipitates when the nitrogen gas was bubbled¹⁹.

After the coprecipitation of Cr(VI) was completed in 1.0 L of 1.0 ng/mL Cr(VI) solution, the atomic absorbance was measured in the concentrated solution varying the amount of the surfactant. As shown in Figure 3, the precipitates were effectively floated with over 1.0 mL mixed solution of each 0.5% surfactant. This corresponds to about 10^{-3} mole ratio to AgCl. Thus, the flotation could be done only with its very small amount.

Bubbling rate of nitrogen gas. The flotation efficiency was dependent upon the bubbling rate of nitrogen gas through fritted porous (No. 40) glass disc in the process of flotation of hydrophobic precipitates. So, the absorbance of chromium was measured with changing the bubbling rate. The maximum absorbance was observed in the range 30-50 mL/min of the rate as shown in Figure 4. All of precipitates could not be floated under 20 mL/min of the bubbling rate. On the other hand, above 70 mL/min of the rate, the foam layer was not so stable because the large size of bubble was formed, and parts of precipitates were redispersed into

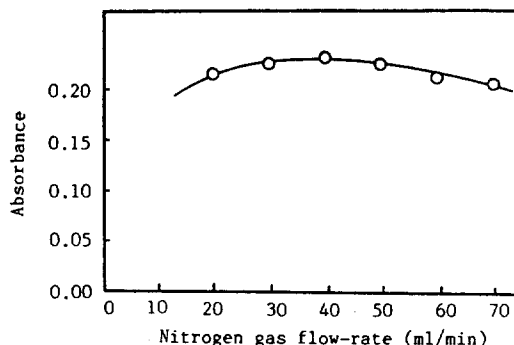


Figure 4. Relationship between nitrogen gas flowrate and flotation efficiency. [Cr(VI)]: 1.0 ng/mL.

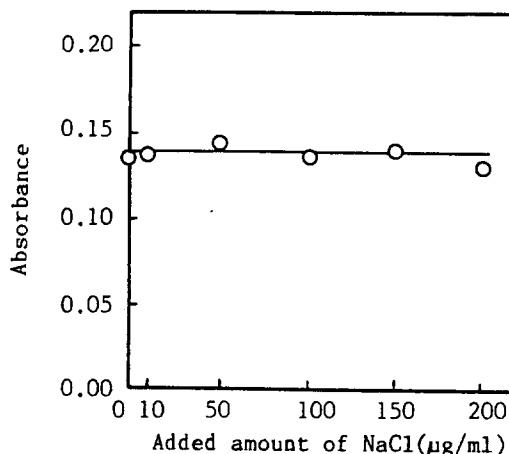


Figure 5. Interfering phenomena of NaCl on the determination of Cr(VI) by graphite furnace AAS. [Cr(VI)]: 20 ng/mL.

the solution. Therefore, the gas was bubbled at 40 mL/min on the flow meter.

Investigation and removal of interferences

Halides of alkali metals. Generally, it has been known that the halides of alkali metals interfered the absorbance measurement of analyte by the electrothermal atomization in a graphite furnace²⁰, especially, their interferences were serious at the short wavelength of resonance line for an analyte²¹. But any interferences of them were not observed in this experiment. Such a phenomenon could be confirmed with NaCl as shown in Figure 5. This was from that the measured 357.9 nm was not so short wavelength.

Trivalent chromium. Cr(III) exists in a natural water together with Cr(VI), and it interferes the determination of Cr(VI) in this method. Especially, the coexistence of Cr(III) causes a serious interference on the absorbance measurement of Cr(VI) because atomic absorption spectrometry cannot distinguish the oxidation states of an element. The serious interference of Cr(III) was observed in this experiment as shown in Figure 6. This fact is caused by the coprecipitation of Cr(III) as Cr(OH)_3 on the AgCl precipitate together with Cr(VI) in a basic solution.

Mullins¹ reported that Cr(III) could be removed from the solution of Cr(III) and Cr(VI) through the filtration of the Cr(III) adsorbed on Fe(OH)_3 by adjusting pH to 7-8 and

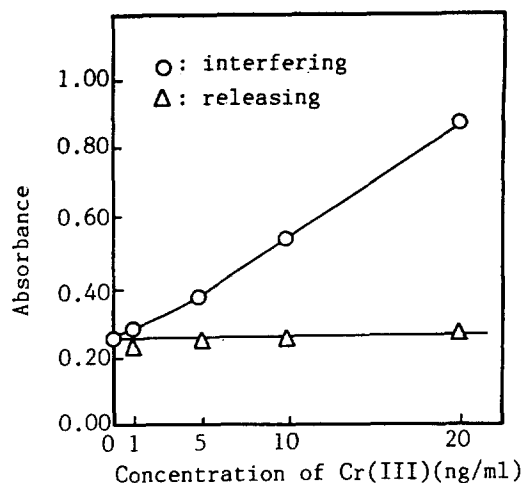


Figure 6. Interference and its release of Cr(III) on the flotation of Cr(VI). [Cr(VI)]: 1.0 ng/mL.

standing more than 4 hours. Kim and Zeitlin⁵ also indicated that hydrated iron(III) oxide was a useful precipitate to remove most of cations from a solution because of its negative charge in a basic solution. Therefore, the hydrated iron(III) oxide was used to remove Cr(III) in this work. That is, after Fe^{3+} was added to the sample solution, it was precipitated as $\text{Fe}(\text{OH})_3$ by making it basic and stirring. The stirring was continued over 1 hour and the solution was stood more than 4 hours. The precipitate of $\text{Fe}(\text{OH})_3$ including Cr(III) was removed by the flotation with mixed surfactant. The elimination of Cr(III) interference by the pre-flotation was confirmed as shown in Figure 6.

Other ions. The interferences of several concomitant cations and anions on the absorbance measurement of Cr(VI) and their elimination were investigated. Generally, the concomitant iron was known to interfere the absorbance measurement of chromium in flame AAS. But the coexistence of Fe^{3+} ion did not cause any problems because the Fe^{3+} ion was simultaneously removed by the pre-flotation in which $\text{Fe}(\text{OH})_3$ was used as coprecipitant. On the other hand, if any Fe^{2+} ion exists in a natural water, then it reduces Cr(VI) by the oxidation of itself to Fe^{3+} so that any problem is not induced on the flotation of Cr(VI).

The coexistence of Mg^{2+} and Al^{3+} ions increased the absorbance of chromium, respectively, as shown in Figure 7a. Especially, the interference of magnesium was caused by the matrix modification of magnesium nitrate to delay the life time of atomized chromium in a graphite furnace²². Therefore, Mg^{2+} and Al^{3+} should be removed if they existed. But they were also coprecipitated together with $\text{Fe}(\text{OH})_3$ in a basic solution and simultaneously removed in pre-flotation. Total interferences and elimination of them can be seen in Figure 7b.

In addition, interferences of other cations and anions such as Pb^{2+} , Cd^{2+} , PO_4^{3-} , CO_3^{2-} , etc. were also investigated. The results were summarized in Table 2.

Organic materials including detergents. The sample to be studied in this experiment was a waste water of this University and it would contain various kinds of organic materials including some detergents. These organic materials happen to make some interferences in the processes of co-

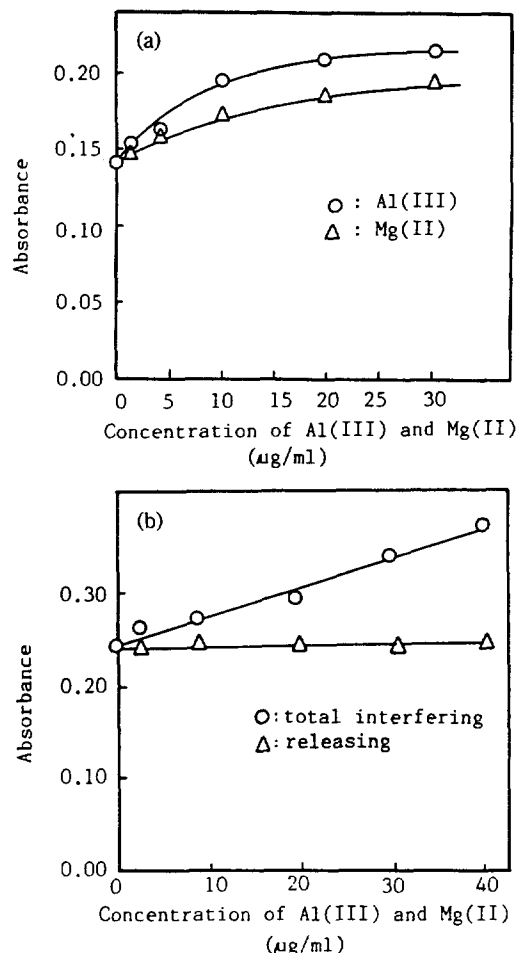


Figure 7. Interferences and their release of Al and Mg. [Cr(VI)]: 1.0 ng/mL. (a) each interference, (b) total interference and release.

Table 2. Interfering Effects of Various Ions on the Determination of Chromium (VI, 20 ng/mL)

Ions	Concentration Range	Interfering effect
Fe^{3+}	0-20 ppm	no effect
Cr^{3+}	0-500 ppb	interfering
Pb^{2+}	0-50 ppm	no effect
Cd^{2+}	0-20 ppm	no effect
Mg^{2+}	0-20 ppm	interfering
Al^{3+}	0-20 ppm	interfering
Na^+	0-100 ppm	no effect
PO_4^{3-}	0-20 ppm	no effect
CO_3^{2-}	0-10 ppm	no effect

precipitation, flotation and absorbance measurement of Cr(VI) so that the interferences as well as their elimination were investigated using a commercial detergent on the behalf of various organic materials.

Each 1.0 L of 1.0 ng/mL Cr(VI) water sample in which the detergent was added was floated at the same conditions as in pre-flotation and the absorbance was measured and plotted against the amount of the detergent added (see Fig-

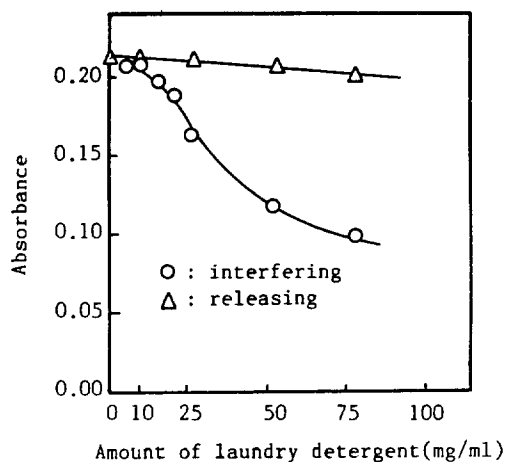


Figure 8. Interference and its release of laundry detergent on the flotation. $[\text{Cr(VI)}]$: 1.0 ng/mL.

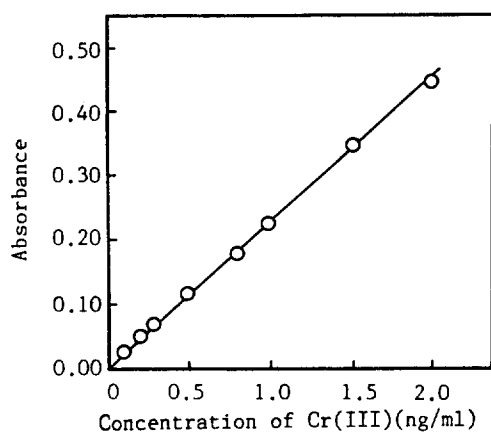


Figure 9. Calibration curve for the determination of Cr(VI).

ure 8). The figure showed that any interference was not observed on the addition of less than 10 mg detergent but the absorbance significantly decreased beyond it. It is due to that AgCl precipitate was so nearly covered with the detergent or organic materials that the coprecipitation of Cr(VI) was not constituted completely.

In order to remove the detergent, a solvent extraction was tried with toluene, MIBK, xylene, etc., but the interference was not removed completely or Cr(VI) was simultaneously extracted so that the decrease of absorbance was not recovered yet. Fortunately, the elimination of their interferences was observed by the pre-flotation of Fe(OH)_3 precipitates which were used to eliminate the interference of Cr(III) (see Figure 8). In consequence, the interference of organic materials could be eliminated through this experimental procedure without any further treatments.

Analytical results

This method was applied for the analysis of waste water of this University. Standard solutions were prepared by dissolving K_2CrO_4 in a distilled water to make the concentration of 0.1–2.0 ng/mL. A calibration curve was obtained after these standard solutions were floated and concentrated by the same method as in a solution sample. Of course, a distilled

Table 3. Analytical Results of Chromium(VI) in Waste Water of Seochang Campus (unit: ng/mL)

Added	Found	Average	Relative standard deviation	Recovery
0.0	0.42	0.41	9.71%	
	0.40			
	0.37			
	0.35			
	0.43			
	0.45			
	0.46			
0.5	0.84	0.84(0.43)	2.92%	86.0%
	0.87			
	0.81			
1.0	1.32	1.32(0.91)	8.33%	91.0%
	1.39			
	1.36			
	1.33			
	1.18			
	1.08			

water treated as above was used as a blank. The curve was linear as shown in Figure 9.

The content of Cr(VI) in a waste water was determined upon the above calibration curve. In order to evaluate the accuracy of this method, recoveries were obtained by analyzing the waste water in which 0.5 and 1.0 ng/mL of Cr(VI) were spiked. As shown in Table 3, the content of Cr(VI) was 0.41 ng/mL in the original waste water, 0.84 and 1.32 ng/mL in the spiked waste water, respectively. Net values spiked were 0.43 and 0.91 ng/mL and their recoveries were 86.0 and 91.0%. Such recoveries are evaluated to be acceptable in the analysis of trace elements. The fact that a relative standard deviation was 9.71% for 7 analyzed results enable to get a relatively reproducible result.

The detection limits were also obtained in a distilled water and the treated water to see how much it was improved through the concentration of Cr(VI) by the flotation. And the detection limit was calculated from the concentration equivalent to the absorbance of two times standard deviation of blank. The value of 0.3 ng/mL in the water was lowered to 0.014 ng/mL through the flotation. This improvement was about 20 times. These results imply that the application of flotation-concentration enables to determine Cr(VI) in a natural water at sub-ng/mL level.

References

1. T. L. Mullins, *Anal. Chim. Acta.*, **165**, 97 (1984).
2. A. D. Shendrikar and P. W. West, *ibid.*, **72**, 91 (1974).
3. K. Yoshimura and S. Oharhi, *Talanta*, **25**, 103 (1978).
4. H. Bergman and K. Hardt, *Fressenius Z. Anal. Chem.*, **297**, 381 (1979).
5. Y. S. Kim and H. Zeitlin, *Separ. Sci.*, **6**, 505 (1978).
6. M. Hiraide, Y. Yoshida, and A. Mizuike, *ibid.*, **81**, 185 (1976).

7. A. Mizuike, M. Hiraide, and T. Kanemitsu, *Japan Analyst*, **26**, 137 (1977).
8. W. J. Williams and A. H. Gillam, *Analyst*, **103**, 1239 (1978).
9. S. Nakashima and M. Yagi, *Anal. Chim. Acta*, **147**, 213 (1983).
10. N. Rothstein and H. Zeitlin, *Anal. Lett.*, **9**, 461 (1976).
11. A. Mizuike and M. Hiraide, *Bull. Chem. Soc. Jpn.*, **48**, 3753 (1975).
12. M. Hiraide and A. Mizuike, *Talanta*, **22**, 539 (1975).
13. M. Hiraide, A. Mizuike, and T. Suzuki, *Japan Analyst*, **18**, 519 (1977).
14. M. Aoyama, T. Hobo, and S. Suzuki, *ibid.*, **30**, 224 (1981).
15. M. Aoyama, T. Hobo, and S. Suzuki, *Anal. Chim. Acta*, **129**, 237 (1981).
16. G. J. de Jong and U. A. Th. Brinkman, *ibid.*, **98**, 243 (1978).
17. K. B. Oldham, *Chem. Educ.*, **51**, 7 (1965).
18. X. Feng and D. E. Ryan, *Anal. Chim. Acta*, **162**, 47 (1984).
19. M. Hiraide and A. Mizuike, *Rev. Chem.*, **VI(2)**, 151 (1982).
20. K. Matsusaki, *Anal. Chim. Acta*, **141**, 233 (1982).
21. R. Kanipayer, *et al.*, *ibid.*, **166**, 39 (1984).
22. C. Veillon, K. Y. Patterson, and N. A. Bryden, *ibid.*, **164**, 67 (1984).

Reactive Intermediate in the Decomposition Reaction of Bis Diazo Compounds

Dae Dong Sung*, Yoo-Mee Park, Kyu Chul Kim, and Dong Kyu Park†

Department of Chemistry, Dong-A University, Pusan 604-714

†Department of Chemistry, Kyungseong University, Pusan 608-736

Received April 13, 1992

Photochemical extrusion reactions of dinitrogen from bis diazo compounds have been carried out by means of laser flash photolysis in argon matrix at low temperature. Photolytic reactions of bis diazo compounds in methanol have been also conducted by using a high-pressure mercury lamp at room temperature. Monocarbenes isolated in the matrix were identified by spectroscopic technique. The spectroscopic result for bis diazo cyclohexanone showed a triplet ketocarbene intermediate at the first step of the loss of nitrogen molecule from the substrate. The continuous decomposition reaction for bis diazo cyclohexanone in methanol at room temperature gave the Wolff rearrangement product.

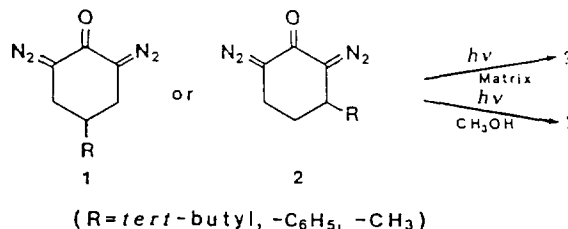
Introduction

The spin state and molecular conformation of a novel hydrocarbon such as dicarbene are of considerable current interest in the area of synthetic organomagnetic materials.¹ Usually the organic molecules have closed-shell electronic structures, *i.e.* they are composed with singlet state of electrons having α -, and β -spins.² Most organic compounds are good electric insulators and are magnetically inactive,³ that is, they have diamagnetic properties since they have the electrons of singlet state.

On the other hand there are some organic molecules that have open-shell electronic structures that contains some spins unpaired.⁴ Many of these molecules have one unpaired electron and exist as a doublet ground state. These species are called free radicals and are known to show paramagnetic properties.⁵ The alignment of spins in molecular systems makes an issue when there is an interaction between two doublet centers, as in diradicals and radical pairs. The Coulombic repulsion between electrons lifts the zeroth-order degeneracy for these chemical species and gives to singlet and triplet states.⁶ Wasserman *et al.*⁷ reported that the dicarbene, consisting of two phenylcarbene units attached to the meta positions of a benzene ring, had a quintet ground state. This

finding established unprecedented macroscopic spins of long-range order⁸ in organic high-spin species and particularly in the possibility of organic ferromagnets.⁹ The series of high-spin hydrocarbons have been detected by spectroscopic measurement for various aromatic poly-carbenes.¹⁰ Despite their investigations, the study of decomposition of bis diazo compound is limited to a few spectroscopic observations.¹¹

A bis diazo compound which is composed of non-Kekulé structure such as bis(diazo)cyclohexanone may be expected to show a different intermediate as triplet or quintet carbene from photolytic observation.



In this paper the decomposition mechanism of bis diazo compound which has cyclohexanone ring system has been investigated by means of photolysis in argon matrix and methanol.

Experimental

General. Proton magnetic resonance ($^1\text{H-NMR}$) spectra were recorded on a Varian XL 400 spectrometer or a Varian XL 200 spectrometer in deuteriochloroform (unless otherwise noted) with tetramethylsilane as an internal standard.

Mass spectra (MS) were obtained from Hewlett-Packard 5996 GC/MS. Infrared absorption (IR) spectra were recorded on a Perkin-Elmer Model 683 grating spectrophotometer. Steady-state ultraviolet-visible (UV/vis) absorption spectra were recorded with UVIKON 940 spectrophotometer. Electron paramagnetic resonance (EPR) spectra were recorded on a Varian Associates E-4 (X-Band) spectrometer. Melting points were determined in the sealed capillary tubes employing a Büchi Schmelzpunkt-bestimmungsapparat. Analytical gas chromatograph (GS) was performed with a Shimadzu GC-RIA gas chromatography equipped with linear-temperature programmer and a flame ionization detector; 1.5-m silanized glass columns containing OV-17 (5%) or SE-30 on dichlorodimethylsilane-treated Chromosorb W and with helium as the carrier gas at 20 psi.

Photolytic reaction was carried on by using a Hanovia 450 W high-pressure mercury lamp at room temperature in methanol. The laser flash photolysis apparatus used was the Laser photonics, LN 1000 Nitrogen Laser System which produces a pulsewidth of 600 ps duration with peak power output in excess of 2 MW and its average intensity limit was $\sim 20 \text{ mJ/cm}^2 \cdot \text{sec}$ up to $50 \text{ mJ/cm}^2 \cdot \text{sec}$ at 355 nm. The rise time of the system was measured as $\cong 5 \text{ ns}$, although this resolution could be achieved in practice using the laser.

The emission spectra were measured as a change in optical density. In a single-pulse irradiation, their optical densities represent the difference between the transient and its stable precursor, e.g., the diazo compound.

In order to measure the lifetime of carbene we have used a sufficiently short pulse at 600 ps to allow direct lifetime measurements based on the fluorescence decay using an Instapec TM-XT detector Model 77160 and Stanford Research Systems Model SR 400 Gated Photon Counting System.

For all of the flash photolytic investigations, the samples of 2,6-bis(diazo)-cyclohexanones were contained in $10 \times 10 \text{ mm}$ (3 mL) graded seal quartz cuvettes. All samples were deaerated by purging with oxygen-free nitrogen.

Materials. 4-*tert*-butylcyclohexanone, 3-methylcyclohexanone, 4-methylcyclohexanone, 4-phenylcyclohexanone, 3-phenylcyclohexanone, isoamyl nitrite and sodium chloride were purchased from Aldrich Company and used without further purification.

Methanol was further purified by the literature method¹² for appropriate spectroscopic research.

4-*tert*-butyl-2,6-Bis(diazo)cyclohexanone. 4-*tert*-Butylcyclohexanone (3.856 g, 25 mmol) dissolved in 25 mL of dry diethyl ether was introduced to a 100 mL three-necked round-bottomed flask equipped with a magnetic stirring bar, a thermometer, a dropping funnel containing 1 mL of 37% hydrochloric acid and a reflux condenser fitted with a argon balloon. While the reaction mixture being stirred, the hydrochloric acid was added slowly during a period of ca. 30 min. the reaction was mildly exothermic, and the temperature was maintained at $5\text{--}10^\circ\text{C}$ in the ice bath by controlling the rate of addition the hydrochloric acid. After addition of the

hydrochloric acid was completed, 7.32 mL of isoamyl nitrite was added slowly during a period of ca. 20 min, while maintaining the temperature at $5\text{--}10^\circ\text{C}$.

The reaction mixture was stirred for a total of 1.5 hr after the addition was completed. And 1 mL of fresh pyridine was added to the reaction mixture. The crystalline was separated from the reaction mixtures by suction filtration and washed with water several times. The product was 4-*tert*-butyl-2,6-(oximino)cyclohexanone: Recrystallization from petroleum ether produced pale brown solid: IR (KBr disk) $3400\text{--}3200$, $1720\text{--}1700$, 1600 , 1580 cm^{-1} , mp. 295°C .

4-*tert*-Butyl-2,6-bis(oximino)cyclohexanone (1.802 g, 8.62 mmol) was placed 500 mL three-necked flask equipped with magnetic stirrer, gas inlet, 50 mL of additional funnel and condenser. Dry nitrogen was slowly through the flask, and 68 mL of 15 N- NH_4OH and 25 mL of 5 N- NaOH were added during ca. 30 min. During this time the reaction mixture was maintained at $10\text{--}20^\circ\text{C}$ in the ice bath. After the addition was completed, then 25 mL of 5% sodium chlorite was added during ca. 10 min. Stirring was continued for 1 hr. The aqueous layer was separated from the ether and then extracted twice with ether. The ether solution was dried over anhydrous Na_2SO_4 for 10 hours, and then the solvent was removed on a vacuum drier. The product was reddish yellow solid: mp. $102\text{--}105^\circ\text{C}$; IR (KBr), 3190 , 2815 , $2100\text{--}2050$, 1610 , 1580 , 1450 , 1280 cm^{-1} , $^1\text{H-NMR}$ (CDCl_3) δ 0.98 (s, 9H), 2.4–2.7 (m, 4H).

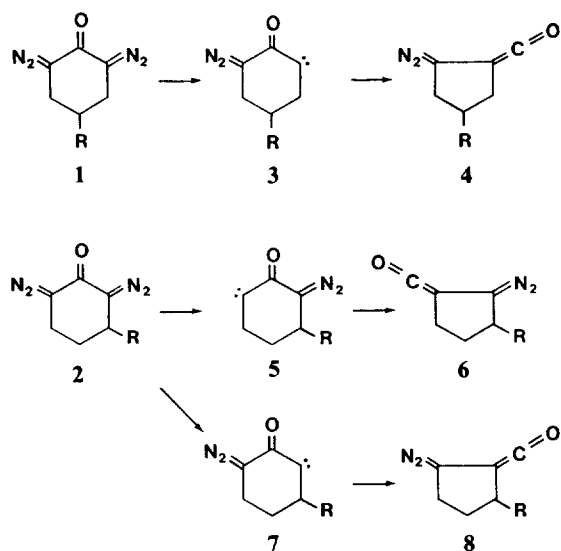
3-Methyl-2,6-Bis(diazo)cyclohexanone. The diazo compound was similarly prepared by substituting 3-methylcyclohexanone for 4-*tert*-butylcyclohexanone. This product (71% after recrystallization from ether/petroleum ether) was red solid. mp. $50\text{--}53^\circ\text{C}$; IR (KBr) 2980 , 2705 , $2100\text{--}2050$, 1580 , 1450 , 1280 cm^{-1} , $^1\text{H-NMR}$ (CDCl_3) δ 1.19 (d, 3H- CH_3), 1.30–1.76 (m, 1H), 1.8–2.1 (m, 1H), 2.64 (d, 2H), 2.8–3.1 (m, 1H).

4-Methyl-2,6-Bis(diazo)cyclohexanone. The diazo compound was similarly prepared as the method 3-methyl-2,6-bis(diazo)cyclohexanone using 4-methylcyclohexanone. The product (76% after recrystallization using ether/petroleum ether) had yellowish red solid and mp. $62\text{--}64^\circ\text{C}$; IR (KBr) 3020 , 2990 , 2705 , $2100\text{--}2050$, 1610 , 1570 , 1450 , 1285 cm^{-1} , $^1\text{H-NMR}$ (CDCl_3) δ 1.02 (s, 3H), 2.5–2.7 (m, 4H).

4-Phenyl-2,6-Bis(diazo)cyclohexanone. The diazo compound was similarly prepared by substituting 4-phenylcyclohexanone for 4-*tert*-butylcyclohexanone. The product (59% after separation from a liquid chromatograph) had a yellow liquid: IR (NaCl) 2980 , 2770 , $2100\text{--}2050$, 1605 , 1580 , 1370 , 1240 cm^{-1} , $^1\text{H-NMR}$ (CDCl_3) δ 2.6–2.8 (m, 4H), 7.4 (s, 5H).

3-Phenyl-2,6-Bis(diazo)cyclohexanone. The diazo compound was similarly prepared as the method 3-phenyl-2,6-bis(diazo)cyclohexanone from 3-phenylcyclohexanone. The product (68% after separation from a liquid chromatograph) had a red-orange viscous oil; IR (NaCl) 3010 , 2995 , 2785 , $2100\text{--}2050$, 1710 , 1620 , 1580 , 1410 cm^{-1} , $^1\text{H-NMR}$ (CDCl_3) δ 1.25–1.28 (m, 2H), 2.42–2.47 (m, 2H), 7.5 (s, 5H).

Low-temperature photolysis. Low-temperature spectra at 10 K were obtained by using a three-window (quartz) optical Dewar filled with liquid helium. the apparatus consists of three components: a refrigeration unit, a vacuum system, and a gas-handling system, and mounted on a movable cart. An Air Products Medel 202 Displex cryogenic refrigeration system, equipped with standard instrumentation



Scheme 1.

skirt and optical spectroscopy shroud Model DMX-IA. All apparatus and experimental technique used in this study of matrix-isolated reactive species have been applied by the method of Hess¹³ and Kreil¹⁴. The sample was dissolved in dry methanol, placed in a long-necked Pyrex cuvet (ca. 3 mL), closed with a septum, and cooled in the liquid helium. After a baseline had been recorded, the sample was irradiated for several minutes in the spectrophotometer with a 450 W high-pressure mercury lamp or the laser beam. During the helium boil off the temperature was controlled by varying the current supplied to a resistance heater in the dewar. The temperature was monitored with a thermocouple and was maintained constant to within 1 degree.

Low-temperature EPR spectrum. The bis(diazo)cyclohexanone of ca. 0.5 mg in argon matrix of ca. 0.5 mL was placed in a quartz tube, helium was bubbled through the solution, and then it was capped with a septum and teflon tape. The sample was cooled to 10 K in a Dewar vessel which was equipped with quartz outer windows and sapphire inner windows and a liquid-helium transfer line, and then irradiated with a Hanovia 450 W high-pressure mercury lamp and the laser beam in the EPR cavity.

Results and Discussion

Spectroscopic behavior of excited ketocarbene.

Irradiation ($\lambda > 274$ nm) of 4-substituted-2,6-bis(diazo)cyclohexanone (1) was performed in argon at 10 K and gave first a diazoketene as shown in Scheme 1.

While irradiation of 2 isolated in argon at same temperature gave two isomers of monodiazoketene (6, 8). Irradiations by various wavelengths (> 416 nm, 415 nm, 364 nm, $\lambda > 274$ nm) were tried to obtain the spectra.

Irradiation by shorter wavelengths of $\lambda > 274$ nm showed only faster conversion of starting material. The diazoketenes (4, 6, 8) were easily identified by the intense band of infrared ketene stretching vibration ($\nu_{C=O}$) at 2118 and 2120 cm^{-1} . Irradiations ($\lambda > 274$ nm, 8 min) of 1 gave a very strong triplet carbene spectra as observed at 10 K by ESR spectroscopy as shown in Figure 1.

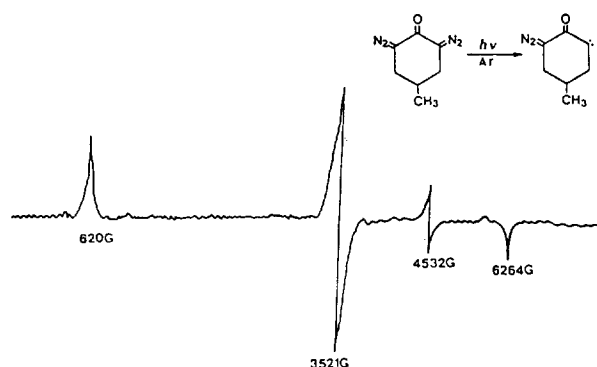
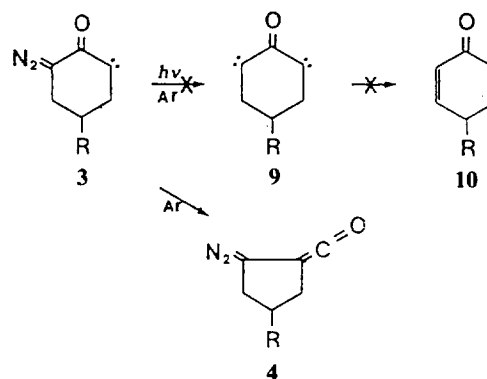


Figure 1. Electron spin resonance spectrum of 4-methyl-2-diazo cyclohexanone carbene (3) at 10 K.



Scheme 2.

Observation of the ESR signal of 5 and 7 also implies that the triplet state is either a minimum energy ground state or a state approaching to zero cal/mol of ground state in argon matrices at 10 K.

Furthermore irradiation by laser beam exhaustively to their triplet absorption species of 3, 5 and 7, the different spectra were not observed such as a quintet spectra at the X band ESR. If the quintet spectra were obtained in case of further irradiation of 3, 5 and 7, the quintet ESR spectra would be shown at the ground state of the dicarbene or at most a few small calories above the ground state. That is, in that case, there is a possibility to yield methyl-1,4-benzoquinone (10) from the quintet species. But ESR spectra are shown only triplet state. Therefore the possibility to produce the product (10) is excluded as shown in Scheme 2.

For the triplet carbene as shown in Figure 1 the zero-field splitting parameter (D/hc) and E/hc term based on the spin Hamiltonian¹⁵ were determined by the magnetic interaction between the unpaired electrons as for 1; ($R = \text{tert-butyl}$), $D/hc = 0.0821$ cm^{-1} , $E/hc = 0.0243$ cm^{-1} , for 1; ($R = \text{Me}$), $D/hc = 0.0823$ cm^{-1} , $E/hc = 0.0241$ cm^{-1} , for 2; ($R = \text{Me}$), $D/hc = 0.0842$ cm^{-1} , $E/hc = 0.0231$ cm^{-1} respectively. The D/hc values for mono carbenes of 2,6-cyclohexanone system are extremely lower than those comparing with other ground state triplet species,⁷ while the values are close to dehydrobenzoquinodimethane (DBQM) like diradical.¹⁶ This observation is supporting the fact that there is no possible Kékulé structure of the quintet dicarbene containing a six membered ring which has a lower multiplicity.¹⁵

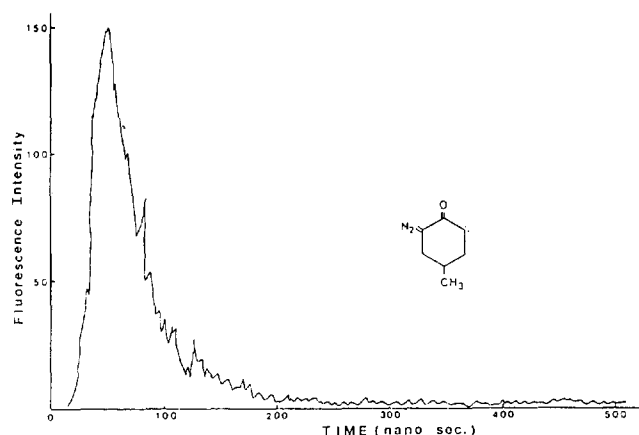
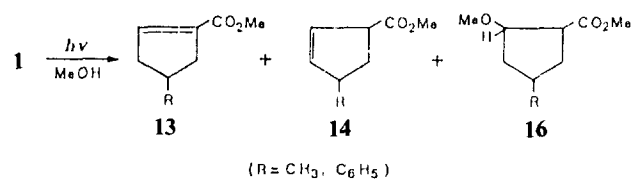


Figure 2. Fluorescence spectrum of excited 4-methyl-2-diazo cyclohexanone carbene (3) produced by excitation of the mono carbene in cyclohexane by 365 nm pulse at 10 K.



Scheme 3.

To find further evidence for the triplet character of mono carbenes (3, 5, 7) laser flash photolysis (LFP) was carried out at 10 K. A fluorescence spectrum obtained from the LFP is shown in Figure 2. The plot of the fluorescent intensity at 365 ± 5 nm as a function of nano second time scale is shown in Figure 2. The excited mono carbene (3) shows triplet-triplet fluorescence emission spectra at 10 K. A similar fluorescence spectra were obtained for 1 (R = *tert* butyl and phenyl) and for 2 (R = methyl and phenyl) as shown in Figure 2 at 45-50 ns. The fluorescence emission spectra were shown to be conformable with the triplet carbene state for 3, 5, and 7.

The spectroscopic behavior for 3-substituted-2,6-bis(diazo) cyclohexanone (2) by using ESR and LFP methods showed a very similar trend of 4-substituted-2,6-bis(diazo)cyclohexanone (1) as triplet ketocarbene intermediate at the first step of the loss of nitrogen molecule from the substrate.

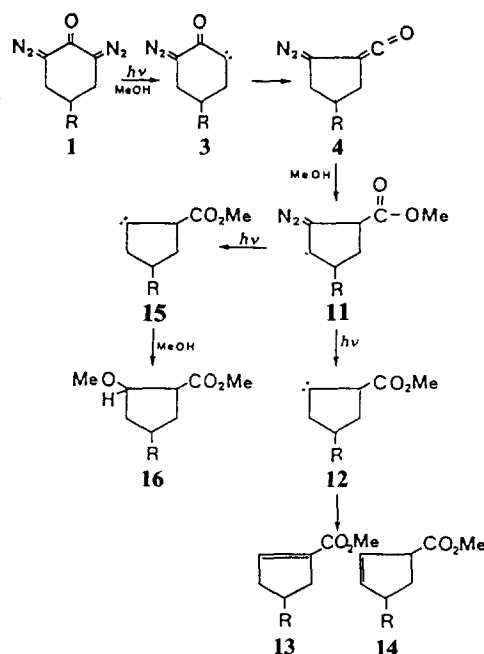
Continuous Decomposition Mechanism for Bis(diazo)cyclohexanone in Methanol. 4-Substituted-2,6-bis(diazo)cyclohexanones (1) have photolysed in methanol using a 450 W high-pressure mercury lamp at room temperature.

3-Methyl-1-methyl cyclopentenecarboxylate (13), 2-methyl-4-methyl cyclopentenecarboxylate (14) and 3-methyl-5-methoxy-1-methyl cyclopentanecarboxylate (16) were obtained as shown Scheme 3 as Wolff rearrangement product.

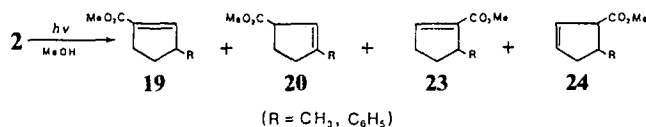
And 3-phenyl substituted 13, 14, and 16 products were obtained by the same photolytic method in methanol as shown in Scheme 3.

The reaction mechanism of the photolyses for 1 in pure methanol could be explained to prove an existence of the triplet carbenes at least in two steps through the photolytic reaction as shown Scheme 4.

Product analyses showed that the product 13 was a good



Scheme 4.



Scheme 5.

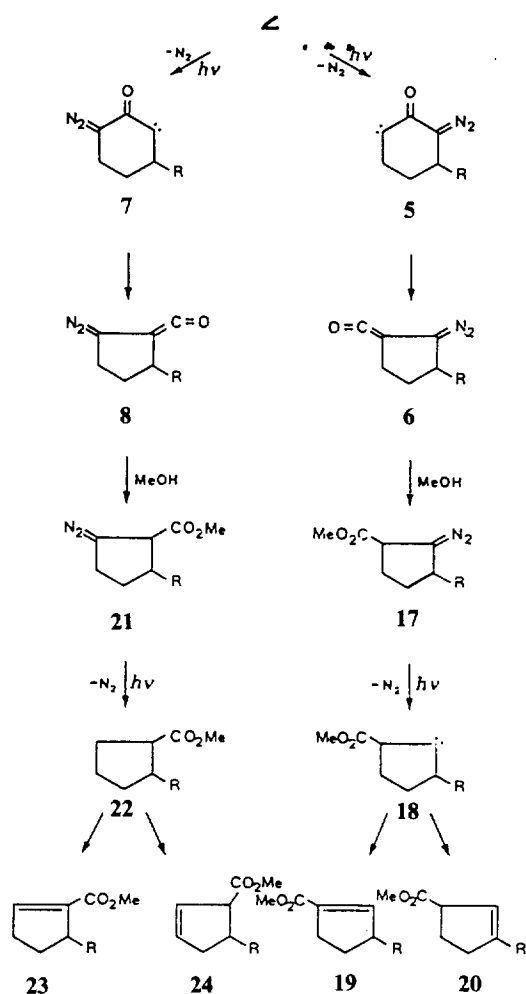
yield comparing with 14 and 16.

Another product analysis carried on the direct and triplet-sensitized photolysis of α -diazocarbonyl compounds by Tomioka¹⁷ to postulate a concerted component occurring from the S-Z conformation and a nonconcerted component occurring from the S-E conformation. The experimental result of Tomioka reveals that the formation of Wolff rearrangement products was caused by triplet-sensitized irradiation.

In our experiments the Wolff rearrangement was observed nevertheless, there was no triplet sensitized conditions which diazo ketone took part in the step of ring contraction. The previous observation of ESR and LFP in this work illustrate that the participation of diazo ketone is excluded between the first step of simple nitrogen loss to give a ketocarbene and the second step of ring contraction to give ketene as shown as 3, 4 in Scheme 4.

3-Substituted-2,6-bis(diazo)cyclohexanones (2) were also photolysed in methanol using a 450 W high-pressure mercury lamp at room temperature. 1-Carbomethoxy-3-methylcyclopentene (19), 3-carbomethoxy-1-methylcyclopentene (20), 2-carbomethoxy-3-methylcyclopentene (23) and 3-carbomethoxy-4-methylcyclopentene (24) were obtained from Wolff rearrangement as shown in Scheme 5. 3-Phenyl substituted 19, 20, 23, and 24 products were also obtained by the same photolytic method in methanol as shown in Scheme 5.

The reaction mechanism of the photolyses for 2 in pure methanol could be also explained to prove an existence of the triplet carbenes in each steps when released the two molecules of nitrogen. Product analyses of the reaction shown in Scheme 5 revealed that the yield of compound



Scheme 6.

19 and **23** were greater than those of **20** and **24**. This trend is similar to the photolysis of **1**. The mechanism and spectroscopic results show that Wolff rearrangement proceeds through the steps of **5**→**6** and **7**→**8** in Scheme 6.

Our results are explainable that the ketocarbene (T_0) of triplet ground-state is produced as the primary photoproduct by photolysis of bis diazo ketone precursor as shown in Figure 3. The moment the ketocarbene (T_0) produced at lower energy state, T_0 might be excited to the higher energy state of the ketocarbene (T_1). The ketocarbene T_1 exists as a higher vibronic state, which rapidly deactivates to different lower vibrational level by intersystem crossing conversion. In that case the intersystem crossing would be carried out nonradiative transition between two vibronic states of different multiplicity¹⁸.

Presumably the singlet states exist three kind of energy states as S_0 , S_{II} and S_{III} on the assumption that two spins occupy in the energy order as shown in Figure 3. The lower two singlet states of ketocarbenes, $S_I(n, \pi^*)$ and $S_{II}(\pi, \pi^*)$ would not convert to T_0 state of ketocarbene in direct irradiation.¹⁹ Because the necessary extrusion energy of the second intersystem crossing can be even more than the energy of the vertical singlet-triplet transition of the carbene.¹⁹ In direct irradiation generally those carbenes which involve an excited state of S_I is ruled a spin-forbidden transition to

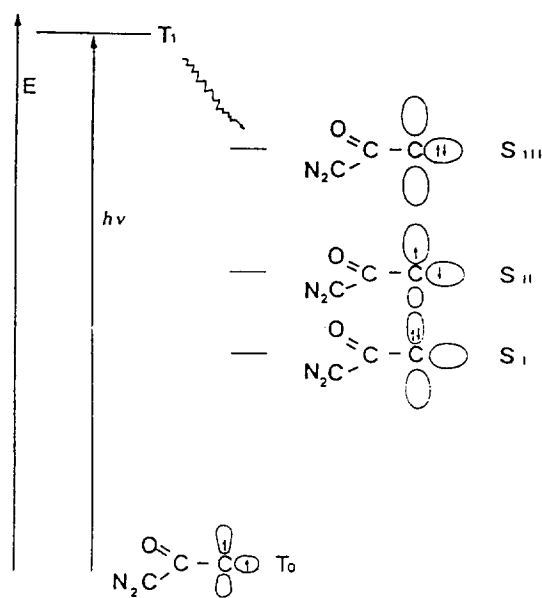


Figure 3.

convert T_0 .²⁰

Our result is satisfied that the conversions of T_0 state→ T_1 state→ S_{III} state occur as shown in Figure 3 since the photochemical reaction was carried on by direct irradiation. However, a different result^{20b} has been reported that the precursors of keto diazo compound is converted from S_I state to T_0 state by the intersystem crossing. In that case the precursors of keto diazo compounds have very different energy and structure compared with our keto diazo compound. If the intersystem crossing of S_I → T_0 easily occurs, the S_I state would exist a state of unreactive species and Wolff rearrangement would not be favorable to occur. Another evidence²¹ has been reported that a concerted Wolff rearrangement proceeds *via* the lowest vibrational state of S_I diazoketone to T_0 state in conformationally mobile systems. Those intermediates of carbene of S_I and T_0 are different from our carbene since the intermediates of carbene are produced from mono diazo compound in comparison with what the carbenes in this experiment are produced from bis diazo compound. Therefore, it is reasonable that stereoelectronic factors in ketocarbenes (**3**, **5** and **7**) preclude ring contraction in the S_I state, thereby leading to trapping of the highly reactive, first-formed ketocarbenes. If a singlet state of S_I is favored to the intersystem crossing, the S_I state could not be oriented the first ring contraction²² because the electronic state of S_I is the conformationally rigid ketocarbenes. Furthermore the singlet state of S_{II} is not appropriate because it does not possess²³ a vacant orbital as shown in Figure 3.

Therefore the Wolff rearrangement in photochemical extrusion reactions of bis diazo compounds (**1** and **2**) was proceeded through from α -diazo ketone to α -diazo ketene, and the step of ring contraction was facilitated by the higher energy singlet state of S_{III} .

Acknowledgement. The present studies were supported by the Ministry of Education of the Republic of Korea through the Basic Science Research Institute Program (BSRI-92-342) and Korea Science and Engineering foundation (91-03-00-07). We thank Dr. Minyung Lee and Dr. Dongho Kim

for their help in obtaining the laser flash photolysis data.

References

1. Y. V. Korshak, A. A. Ovchinnikov, A. M. Shapino, T. V. Medvedeva, and V. N. Spector, *JEPT Lett (Engl. Transl.)*, **43**, 399 (1986); I. Fujita, T. Yoshio, T. Takeji, T. Kinoshita, and K. Itoh, *J. Am. Chem. Soc.*, **112**, 4074 (1990); J. B. Torrance, S. Oostra, and A. Nazzari, *Synth. Met.*, **19**, 709 (1987); J. S. Miller, A. J. Epstein, and W. M. Reiff, *Chem. Rev.*, **88**, 207 (1988).
2. Y. Teki, T. Takui, K. Itoh, H. Iwamura, and K. Kobayashi, *J. Am. Chem. Soc.*, **108**, 2147 (1986).
3. H. Iwamura, *Adv. Phys. Org. Chem.*, **26**, 180 (1990).
4. W. T. Borden, "Diradicals", Wiley, New York Chap 1, (1982).
5. D. Bethell and M. R. Brinkman, *Adv. Phys. Org. Chem.*, **10**, 53 (1973).
6. A. R. Lepley and G. L. Closs, "Chemically Induced Magnetic Polarization" Wiley, New York (1973).
7. E. Wasserman, R. W. Murray, W. A. Yager, A. M. Trozzolo, and G. Smolinsky, *J. Am. Chem. Soc.*, **89**, 5076 (1967).
8. J. Brickman and G. Kothe, *J. Chem. Phys.*, **59**, 2807 (1973); T. Takui and K. Itoh, *Chem. Phys. Lett.*, **50**, 1251 (1978).
9. N. Mataga, *Theor. Chim. Acta.*, **10**, 372 (1968); A. A. Ovchinnikov, *Theor. Chim. Acta.*, **47**, 297 (1978); M. Schworer, R. A. Huber, and W. Hartl, *Chem. Phys. Lett.*, **55**, 97 (1981).
10. T. Takui and K. Itoh, *Chem. Phys. Lett.*, **19**, 120 (1973); K. Itoh, *Pure. Appl. Chem.*, **50**, 1251 (1978); Y. Teki, T. Takui, H. Yagi, K. Itoh, and H. Iwamura, *J. Chem. Phys.*, **83**, 539 (1985); S. Murata, T. Sugawara, and H. Iwamura, *J. Am. Chem. Soc.*, **109**, 1266 (1987).
11. R. W. Murray and M. L. Kaplan, *J. Am. Chem. Soc.*, **88**, 3527 (1966); H. Meier and I. Menzer, *Synthesis*, 215 (1971).
12. E. C. Evers and A. G. Knox, *J. Am. Chem. Soc.*, **73**, 1739 (1951).
13. T. C. Hess, Ph. D. Dissertation, University of California, Los Angeles, CA (1978).
14. C. L. Kreil, Ph. D. Dissertation, University of California, Los Angeles, CA (1983).
15. K. Itoh, *Pure. Appl. Chem.*, **50**, 1251 (1978); H. Iwamura, *Pure. Appl. Chem.*, **59**, 1595 (1987).
16. K. Itoh, *Chem. Phys. Lett.*, **1**, 235 (1967).
17. H. Tomioka, H. Okuno, and Y. Izawa, *J. Org. Chem.*, **45**, 5278 (1980); H. Tomioka, M. Kondo, and Y. Izawa, **46**, 1090 (1981).
18. J. Kopecky, "Organic Photochemistry: A Visual Approach", VCH Publishers, Inc., 33 (1992).
19. For reviews of the photochemistry of diazo compound, see: (a) H. Dürr, In "Methoden der Organischen Chemie (Houben-Weyl)." G. Thieme: Stuttgart, Vol. **4/5b**, 1158 (1975); (b) H. Dürr, *Topics Curr. Chem.*, **55**, 87 (1976); (c) M. Regitz and G. Maas, "Diazo compounds: Properties and Synthesis", Academic, New York (1986); (c) Y. Z. Li and G. B. Schuster, *J. Org. Chem.*, **52**, 4460 (1987).
20. (a) H. Meier and K. P. Zeller, *Angew. Chem. Int. Ed. Engl.*, **14**, 32 (1975); (b) W. Ando, In "The Chemistry of the Diazonium and Diazo Group", S. Patai ed., Wiley, New York, Part 1, 458 (1978); (c) M. Regitz and G. Mass, "Diazo compounds: Properties and Synthesis", Academic Press, Orlando, Florida, 185 (1986).
21. C. Marfisi, P. Verlaque, D. Davidovics, J. Pourcin, L. Pizzala, J.-P. Acard, and H. Bodot, *J. Org. Chem.*, **48**, 533 (1983).
22. W. J. Bouma, R. H. Nobes, L. Radom, and C. E. Woodward, *J. Org. Chem.*, **47**, 1869 (1982).
23. S.-J. Chang, B. K. Ravi Shankar, and H. Shechter, *J. Org. Chem.*, **47**, 4226 (1982).

Observation of Electronic Emission Spectra of CH₃S

Sang Kuk Lee

Department of Chemistry, College of Natural Sciences, Pusan National University, Pusan 609-735

Received January 13, 1993

The combination of Fourier Transform spectroscopy with a technique of supersonic expansion has been employed to examine the vibronic structure of the transition $A^2A_1 \rightarrow X^2E$ of CH₃S radical. CH₃S was produced by an electric *dc* discharge of the precursor (CH₃)₂S. The emission spectrum of CH₃S shows extensive progressions of CS stretching frequencies in the transitions. The molecular parameters describing the vibrational structure of CH₃S have been determined with high accuracy from the analysis of the emission spectrum.

Introduction

For a long time, alkylthio radicals (RS·) have been reported¹⁻³ to be an intermediate in combustion and atmospheric

chemistry of organosulfur compounds. These compounds also play an important role in the atmospheric sulfur cycle and contribute to the acidic rain problem. Particularly, CH₃S is considered an important intermediate in oxidative reaction