seem to be comparable with $\Delta G^\circ_{\text{intrinsic}}$ for other compounds.[21] Thus, a conformational change of diEG diethers may be induced by the hydrophobic interactions between the two alkyl chains in water. Two views of conformation A for the diEG dibutyl ether are shown in Figure 4. This seems to be the most probable conformation, since this conformation may be stabilized by hydrogen bonding of two terminal oxygen atoms ($d_{O-O} = 4.80$ Å) with a water molecule while $\theta_2 = -120°$ and $\theta_7 = 120°$ for conformations B, C, and D are not stable torsional angles.[21]

For the conformations of EG diesters and diethers in water, too many possibilities can be considered and two or more conformers may coexist in equilibrium. In crystals of 1,2-dilauroylphosphatidylethanolamine, the two lauroyl chains are parallel and the distance between them is 4.8 Å.[22] Although this compound has a structure similar to EG diesters, this distance is too small to explain the present result (Table II).

Scope and Limitations of the Present Work. For the determination of S, two assumptions are made: one is the assumption that water is a spherical molecule. A nonspherical water molecule is more realistic[23] but then there emerges uncertainty about the orientation of the water molecule around a solute molecule. Second, only the first hydration layer is taken into account but actually the hydration at the surface of an alkane molecule forms multilayers, called an iceberg.

Recently, the gauche/trans ratio of *n*-butane in water was predicted by microscopic theories based on an integral equation[24] and Monte Carlo method[25] for liquids. However, this ratio for *n*-butane in water has not yet been determined experimentally. In this work, an alkyl chain is assumed to be in all-trans conformation. As the alkyl chain length decreases, the population of the all-trans conformer increases. Since we deal with short-chain ethers and esters, this assumption will be permitted as a first approximation. On the basis of the present results, four possible conformations of diEG diethers in Table I can be considered and conformation A seems to be the most stable conformation. Spectroscopic studies are underway to confirm this conformation.

By using the present results, we can predict the values of cmc,[1] C_w, and P[3] and the conformations of double alkyl chain compounds which are difficult to determine experimentally. For example, the cmc's of diacylphosphatidylcholines[1] and the P values of dialkyl barbiturates can be predicted more accurately by taking into consideration such interactions.[3]

Acknowledgment. Thanks are due to Dr. R. B. Hermann for kindly providing the program MOLAREA and to Miss S. Kato for her assistance.

Registry No. 1-Octanol, 111-87-5; dimethyl ethylene glycol, 110-71-4; diethyl ethylene glycol, 629-14-1; dibutyl ethylene glycol, 112-48-1; diacetate ethylene glycol, 111-55-7; dibutyrate ethylene glycol, 105-72-6; ethyl diethylene glycol, 111-90-0; butyl diethylene glycol, 112-34-5; hexyl diethylene glycol, 112-59-4; dimethyl diethylene glycol, 111-96-6; diethyl diethylene glycol, 112-36-7; dibutyl diethylene glycol, 112-73-2; dipropionate ethylene glycol, 123-80-8.

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Photolysis of 3-Bromo-3-methyldiazirine

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The photolysis at 354 nm of 3-bromo-3-methyldiazirine in gas phase has been studied. After a careful search of the various possibilities we have found that all available evidence points toward the intermediary formation of hot vinyl bromide, presumably via isomerization of the corresponding carbene. Its unimolecular decomposition can take place by two different paths: one is the molecular detachment of HBr and the other the radical scission of the C–Br bond. This last way of radical formation is responsible for the apparently confusing experimental data. According to our results the activation energy for the radical decomposition is closer to that of the molecular detachment than previously thought.

Introduction

The work reported in this paper represents a continuation of our efforts to determine the nature of the processes occurring in the gas-phase photolysis of diazoalkanes and their cyclic isomers diazirines (see ref 1 and references therein). The subject has been recently reviewed by Liu.[2] The study of the partitioning of energy which takes place upon decomposition has shown some defined trends.[3] While the photodecomposition of diazo compounds seems to take place directly in one step from the electronic state reached by the transition, the photolysis of diazirines is more complicated and probably at least one step in the dissociative process is a function of statistical factors.[4]

One of the controversial points about the mechanism of diazirine gas-phase decomposition is the participation of diazo compounds as reaction intermediaries. This participation suggested by Amrich and Bell in the early 1960s[5] was soon disregarded by Moore and

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0022-3654/84/2088-5790$01.50/0

Pimentel.[6] However, more recently Liu and Jennings[7] confirmed the intermediacy of the corresponding diazo compounds in the liquid-phase thermolysis of 3-phenyl-3-*n*-butyldiazirine and 3-phenyl-3-methyldiazirine, and some evidence of participation in the gas-phase photolysis of 3-chloro-3-methyldiazirine was given by Frey[8] and Penny. Theoretical work is also in favor of this intermediacy.[9]

The present study with 3-bromo-3-methyldiazirine was undertaken for two purposes: (1) to determine the effects of the electronegative and bulky bromine atom on the photodecomposition reaction mechanism and (2) to explore the possibilities of obtaining information about the input energy distribution functions from the experimental decomposition data.

Experimental Section

Synthesis of 3-Bromo-3-methyldiazirine. 3-Bromo-3-methyldiazirine (BMD) was prepared by halogenation of acetamidine hydrochloride by oxidation with sodium hypobromite in the presence of lithium bromide. The method was essentially that described by Graham.[10]

The product was swept from the reaction mixture in a stream of nitrogen; the stream was passed through a trap (cooled at 0 °C) and a tube packed with sodium hydroxide pellets. The diazirine was collected in a double trap cooled at −126 °C (methylcyclohexane/liquid nitrogen slush). Final purification was achieved by repeated trap to trap distillation from −78 °C (dry ice/acetone) to −126 °C (methylcyclohexane/liquid nitrogen slush). The hazards involved in freezing diazirines at −198 °C should be remembered.[11] The process was continued until the impurities analyzed by GC and absorption spectroscopy were below the 5% level. The diazirine was identified by its IR, UV, and mass spectra which have been previously reported.[12]

The diazirine was handled in a grease and mercury-free vacuum line. Pressure was monitored by a M.K.S. Model 221 A transducer.

Analysis. The systematic quantitative analysis of the photolysis products (i.e. nitrogen vinyl bromide, ethylene, and acetylene) and diazirine was made by gas chromatography using a H&P 5750 gas chromatograph provided with flame and hot-wire detectors. Quantitative analyses were performed at room temperature with a 2 m × 0.64 cm column of 25% dimethylsulfolane on Chromosorb P NAW. The qualitative and quantitative analyses of bimolecular reaction products (i.e. 1,1- and 1,2-dibromoethane, tribromomethane, and dibromomethane) required additional techniques. A MS30 A.E.I. was used for mass spectrometry; access to the ionization chamber was through a molecular membrane separator in the particular configuration available. A Pye Unicam LC3-XP with UV and refractive detectors was used for high-pressure liquid chromatography. A combined H&P 5790 gas chromatograph and 5970 mass detector was also used for products analysis. All the techniques described above plus UV and IR spectroscopies were used in the attempts to find other possible reaction products.

Photolyses. Preparative photolyses were carried out at room temperature in cylindrical Pyrex vessels of about 400 cm^3 provided with a water-cooled jacket. The surface to volume ratio was around 1.5 cm^{-1}. The light source was a Hanovia Model 654 A 36 mercury lamp.

The systematic determination of pressure effects on photolysis products was carried out using cylindrical glass cells of 10-cm length and of 2.5-cm external diameter with cemented quartz windows. In some cases an all-fused quartz cell of the same dimensions was used. Experiments were performed at 354 nm, to 20%–40% BMD decomposition. A Bausch & Lomb "high-intensity" monochromator (band-pass 10 nm) was used to select the required wavelength.

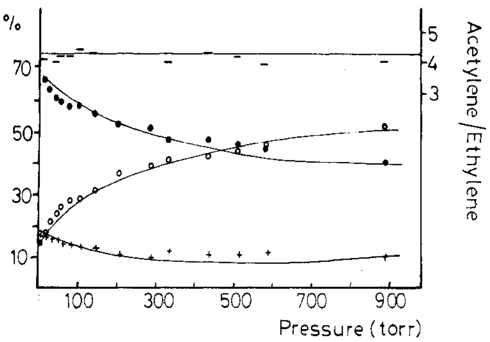

Figure 1. Photolysis of 3-bromo-3-methyldiazirine in the presence of (Z)-2-butene at 354 nm. Plot of the percentage of products (the sum of all photolysis products found in the gas phase) against total pressure (torr): acetylene (●), ethylene (+), vinyl bromide (○) and acetylene/ethylene (–). Ratio BMD:(Z)-2-butene between 1:10 and 1:20.

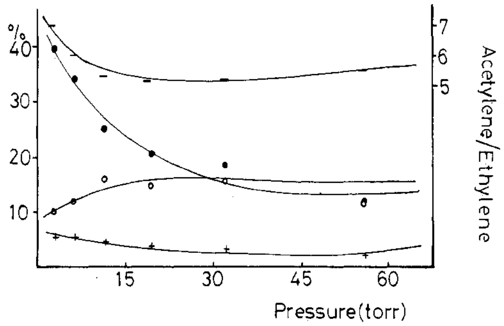

Figure 2. Photolysis of pure 3-bromo-3-methyldiazirine at 354 nm. Plot of the percentage of products (decomposed diazirine) against initial pressure (torr): acetylene (●), ethylene (+), vinyl bromide (○), and acetylene/ethylene [–].

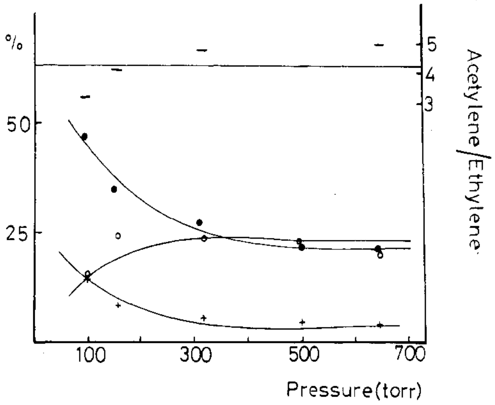

Figure 3. Photolysis of 3-bromo-3-methyldiazirine in the presence of (Z)-2-butene at 354 nm. Plot of the percentage of products (decomposed diazirine) against initial pressure (torr): acetylene (●), ethylene (+), vinyl bromide (○), and acetylene/ethylene (–). Ratio BMD:(Z)-2-butene between 1:10 and 1:20.

Quantum Yield. The quantum yield for decomposition of BMD was determined at room temperature with 354-nm radiation. In an all-fused quartz cell of volume 44.4 cm^3 we introduced known pressures of BMD. The incident and transmitted light were measured with an International Light Model IL 700 A calibrated radiometer. The obtained quantum yield was $\phi_D = 0.9 \pm 0.15$.

Results and Discussion

The major products of photolysis in gas phase detected by gas chromatography were acetylene, ethylene, and vinyl bromide. Products in condensed phase were also detected as it will be described later.

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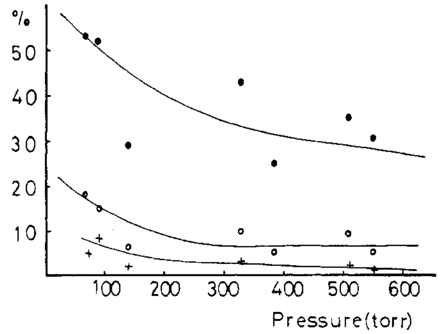


Figure 4. Photolysis of 3-bromo-3-methyldiazirine in the presence of nitrogen at 354 nm. Plot of the percentage of products (decomposed diazirine) against initial pressure (torr): acetylene (●), ethylene (+), and vinyl bromide (○). Ratio BMD:N_2 between 1:10 and 1:30.

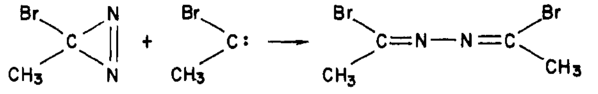
TABLE I: Photolysis of 3-Bromo-3-methyldiazirine at 354 nm with Initially Added Vinyl Bromide[a]

initial BMD	added VB	analyzed VB after photolysis
7.4×10^{-6}	3.4×10^{-5}	3.0×10^{-5}
6.3×10^{-6}	3.9×10^{-5}	3.6×10^{-5}
1.8×10^{-5}	4.6×10^{-6}	4.0×10^{-6}
1.4×10^{-5}	8.1×10^{-7}	8.0×10^{-7}
1.3×10^{-5}	6.6×10^{-7}	6.7×10^{-7}
1.6×10^{-5}	4.6×10^{-7}	6.6×10^{-7}

[a] All amounts are in moles. Photolysis time and other experimental conditions are similar to those used in standard experiments.

Typical results are represented in Figure 1, where the percentages of the major products, given as the sum of photolysis products, are plotted against total pressure and the ratio acetylene/ethylene for the photolysis of 3-bromo-3-methyldiazirine at 354 nm in the presence of (*Z*)-2-butene. The products pressure dependence is typical of a unimolecular decomposition of "hot" vinyl bromide (VB). However, when the products percentage was referred to the decomposed BMD carefully measured by GC (diazirine disappearance and nitrogen formation) and UV spectrophotometry (diazirine), all data being coincident, the results showed a considerable deficit of material (see Figures 2–4).

Potential sources of low vapor pressure products were studied. One of these was the formation of the corresponding azine.



The azine's formation in the thermolysis of diazirines in liquid phase has been well documented.[2,7b,13] However, no evidence of azine formation was found by using GC and MS techniques. Additional experimental evidence against this possibility is the correspondence found between the amount of diazirine decomposed and the nitrogen formed, both of them independently determined.

The possible polymerization of VB was studied. The introduction of known amounts of VB in the cell previous to the photolysis showed that the amounts introduced were only very slightly recovered unchanged (see Table I); therefore, an eventual VB massive polymerization was discarded as a plausible explanation for the important material deficit.

As a consequence of these results, a possible dependence of the products' distribution on conversion (i.e. photolysis time) was studied. The results are shown in Figures 5 and 6. While the ratio acetylene/vinyl bromide does not appreciably depend on conversion when (*Z*)-2-butene is used as the colliding gas, there exists a clear dependence in the case of nitrogen. These effects have been ascribed to a more important participation of a radical mechanism in this second case (see below).

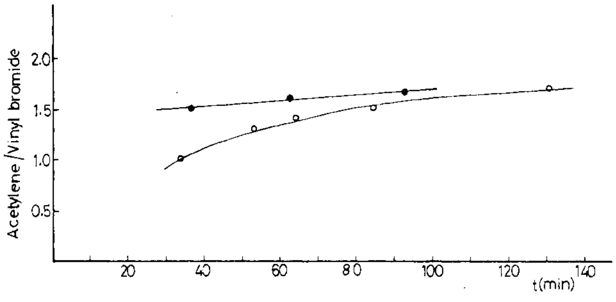


Figure 5. Influence of the irradiation time (conversion). Photolysis of 3-bromo-3-methyldiazirine at 354 nm in the presence of (*Z*)-2-butene at two different total pressures, 248 torr (●) and 227 torr (○). Plot of the acetylene/VB ratio against irradiation time.

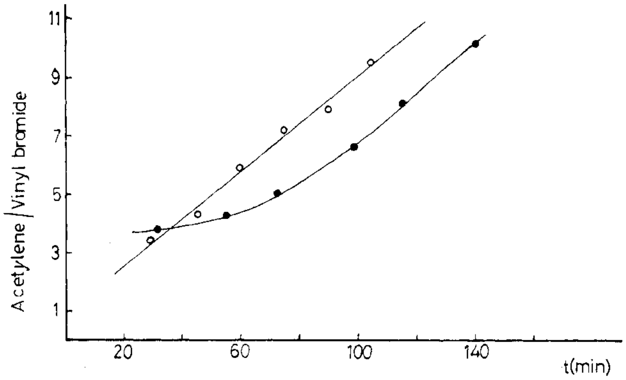


Figure 6. Influence of the irradiation time (conversion). Photolysis of 3-bromo-3-methyldiazirine at 354 nm in the presence of nitrogen at two different total pressures, 331 torr (●) and 356 torr (○). Plot of the acetylene/vinyl bromide ratio against irradiation time.

TABLE II: Photolysis of BMD with O_2 at 354 nm[a]

initial BMD, torr	acetylene found,[b] %	initial BMD, torr	acetylene found,[b] %
73	39.4	442	34.6
141.3	25.0	482	27.4
384.6	20.0		

[a] Ethylene and vinyl bromide are zero within our detection limits (below 2% in three experiments). Ratio BMD/O_2 between 1:10 and 1:30. [b] Refers to diazirine decomposed in the photolysis.

Oxygen exerts also a pronounced effect on the diazirine photolysis. Its presence leads to the total disappearance of ethylene and VB from the reaction products (Table II). In accordance with the above-mentioned participation of a radical mechanism, the vinyl radical (precursor of ethylene) should be effectively scavenged by molecular oxygen. Apparently, oxygen also makes possible VB attack by secondary radical dark reactions.

Possible effects of oxygen on the primary photodecomposition of the diazirine were studied and neglected. Identical amounts of diazirine photolyzed under the same conditions in the presence of similar amounts of either nitrogen or oxygen showed equal, within experimental error, amounts of decomposed diazirine.

Washing the walls of a fused quartz cell with hexane right after the photolysis and analyzing the solutions by HPLC and MS allowed the identification of traces of dibromethane, 1,1-dibromoethane, 1,2-dibromoethane, and tribromoethane. Semiquantitative analysis showed that the inclusion of these compounds in the material balance calculations gave correct results. The above experimental data point out that the photolysis mechanism of this diazirine is more complex than reported previously.[4a,14] Particularly, the presence of ethylene and polybrominated compounds among the reaction products indicates that other processes, besides the molecular formation of acetylene and HBr, play a role in the overall diazirine decomposition.

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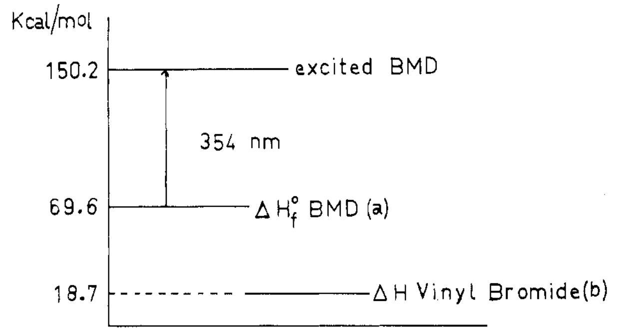
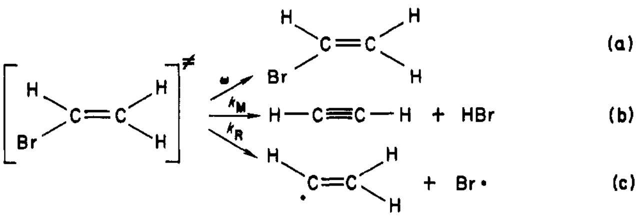
(14) Maeda, Y.; Ingold, K. U. *J. Am. Chem. Soc.* **1978**, *101*, 837.

Chart I. Thermochemical Data



[a] From ref 4a. [b] From ref 24.

According to these results a tentative mechanism for the VB unimolecular decomposition could be written as



Path a represents the ordinary collisional stabilization at the collision frequency ω, path b the molecular detachment of HBr, and path c the radical scission of the C–Br bond that produces atomic bromine and the vinyl radical.

Literature data[15] suggest that the participation of the radical pathway should be very small. However, these data (even those obtained at high temperatures) correspond to average excess energies, $\langle E \rangle_v$ of the hot VB, much lower than those obtained in our experiments. Thus, the average vibrational excess energy calculated from using the frequencies model of VB described in Appendix 1 gives a value of 17 kcal·mol^{-1} for $\langle E \rangle_v$ at 1600 K, the higher temperature used in the above-mentioned thermolysis. In our case (see Chart I) the available energy for partitioning between VB and nitrogen is ~132 kcal·mol^{-1} at 354 mm. Taking a very conservative factor of 0.5 as the fraction of energy channeled into VB, its $\langle E \rangle_v$ is still higher by a factor of at least 4 than the value reached in the shock wave experiments mentioned.

The relevance of the excess energy carried by the VB is evidenced by theoretical RRKM calculations of the microscopic rate constants for different energies (see Figure 7 and Appendix 1). The corresponding curves show that at low energies molecular decomposition is clearly predominant, but at energies around ~100 kcal·mol^{-1} the curves cross and the difference between them is in general smaller than that at lower energies. However, it should be emphasized that the curve obtained for the molecular decomposition has been constructed from sound Arrhenius parameters and therefore should be considered reliable within theory limitations. On the other hand, the other curve is based on crude estimations and therefore considered of only semiquantitative accuracy. In spite of these limitations we think that the curves in Figure 7 are representative of general energy effects on two competing reactions, one with a lower Arrhenius preexponential factor and activation energy than the other.

The formation of ethylene was ascribed to secondary reactions of the vinyl radical formed by pathway c:

(a) disproportionation:

$$2CH_2{=}CH\cdot \rightarrow C_2H_2 + C_2H_4$$

(b) hydrogen abstraction:

$$RH + CH_2{=}CH\cdot \rightarrow R\cdot + C_2H_4$$

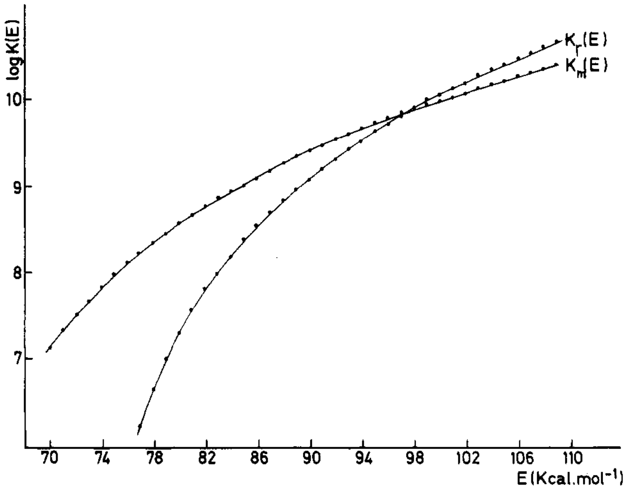
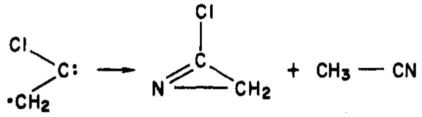


Figure 7. Theoretical microscopic energy-dependent rate constants $k_M(E)$ and $k_R(E)$ for the two paths of vinyl bromide decomposition plotted against energy.

In the absence of a proper hydrogen donor (i.e. (*Z*)-2-butene), BMD itself could have acted as such. However, a similar diazirinyl radical gives[14,16] two identifiable products



which have not been found in our case. More evidence against significative participation of the diazirinyl radical as well as other diazirine bimolecular reactions will be given later.

This low hydrogen abstraction reactivity of the vinyl radical is far from the case where the radical is formed in the photolysis of diazo-*n*-propane[17] where practically all the radical formed abstracts hydrogen. The fact that in the present case the radical should be formed practically cold may explain the differences in reactivity found.

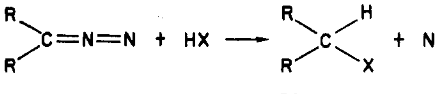
The confirmed absence of butadiene rules out the participation of the recombination reaction:

$$2CH_2{=}CH\cdot \rightarrow CH_2{=}CH{-}CH{=}CH_2$$

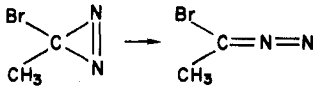
Further evidence against bimolecular processes involving diazirine will be given later.

The formation of the polybrominated products can be explained for by at least three different paths: the intermediacy of the corresponding diazo compound, the participation of the carbene, and the secondary dark radical reactions.

The reaction of diazomethane with hydrogen halides is well established:[18]



In our case diazirine isomerization[7,9] (see Introduction) could give the diazo compound



However, this diazo compound would have to live long enough to collide with the low proportion of HBr molecules present in the medium (formed from path b in the unimolecular decompo-

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(15) (a) Lippiatt, J. M.; Wells, D. E. *Dyn. Mass. Spectrom.* **1976**, *4*, 273. (b) Saito, K.; et al. *Bull. Chem. Soc Jpn.* **1979**, *52*, 3507.

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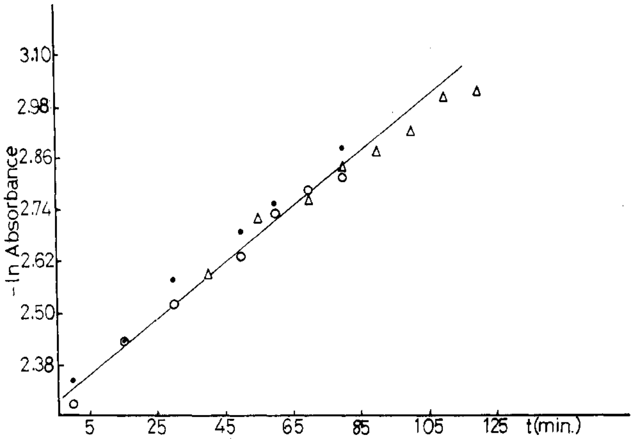


Figure 8. Relative quantum yields. Photolysis at 354 nm of pure 3-bromo-3-methyldiazirine (●), with sulfur hexafluoride (○), and with (*Z*)-2-butene (△). Plot of diazirine concentration disappearance (as the logarithm of its absorbance) against time.

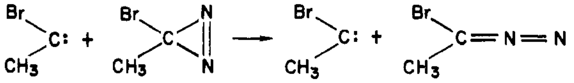
TABLE III: Photolysis of BMD Pure and with Initially Added HBr at 354 nm

initial composition[a]	initial total pressure	sum of gas-phase recovered products[b]
BMD	5	55
BMD + HBr	29	30
BMD + SF_6	680	40
BMD + HBr + SF_6	680	40

[a] Ratios: BMD:HBr, 1:5; BMD:SF_6, 1:70; BMD:HBr:SF_6, 1:3:70. [b] Acetylene, ethylene, and vinyl bromide.

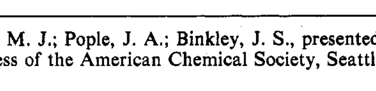
sition of VB and perhaps also present as an impurity in the synthesis of BMD). The high excess energy (~80 kcal·mol^{-1}) that the molecule would have to bear initially, together with its low-energy barrier for decomposition, makes this mechanism very unlikely (see ref 8) for a discussion on the corresponding isomerization in the related photodecomposition of 3-chloro-3-methyldiazirine).

These problems could be eliminated if the diazo compound would have been formed cold by the reaction



This reaction would require a carbene with life long enough to undergo molecular collisions. Recent results about carbene stabilization by electron-donor groups[19,20] favor this hypothesis. However, this reaction would increase the overall quantum yield of diazirine decomposition over the expected value of one. Furthermore, it would make the quantum yield pressure dependent. Experimentally, we have obtained $\phi = 0.9 \pm 0.15$ and, what is more significant, no pressure dependence. Alternative photolysis of identical amounts of BMD with and without added SF_6 and (*Z*)-2-butene (see Figure 8) showed no pressure dependence of the amounts of BMD decomposed, and these experimental results ruled out important participation of any bimolecular reaction involving diazirine itself.

The direct insertion of hydrogen bromide on the carbene is an alternative possibility for the formation of 1,1-dibromethane:



$$\mathrm{Br(CH_3)C\colon + HBr \longrightarrow Br_2HC{-}CH_3}$$

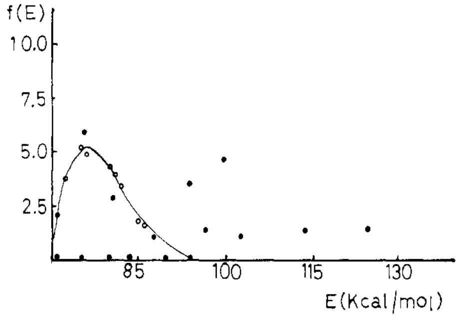
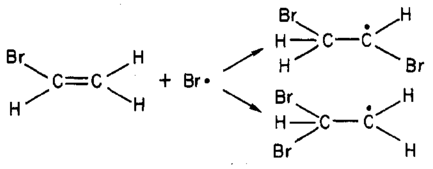


Figure 9. Photolysis of pure 3-bromo-3-methyldiazirine at 354 nm. Deconvoluted energy distribution functions: (○) supposing that all high boiling products are produced from cold vinyl bromide by secondary radical reactions: $D/(D + S) = [C_2H_2 + C_2H_4]/[\mathrm{BMD}]$ disappeared; (●) supposing an earlier reaction which does not affect the radio (see text): $D/(D + S) = [C_2H_2 + C_2H_4)/[C_2H_2 + C_2H_4 + C_2H_3Br]$.

However, this reaction would have to compete with the carbene isomerization. Therefore, at higher pressures the collisional carbene stabilization should favor the bimolecular reaction. Experiments with added HBr at low and high pressures of SF_6 (Table III) showed no significant changes in product distribution, ruling out any important participation of this reaction.

Finally, we are going to discuss the possible radical dark reactions. Bromine atoms may react with VB to give the following radicals:



Further abstraction or recombination reactions could give the identified products:

$$Br_2C_2H_3\cdot \xrightarrow{HR} Br_2C_2H_4 + R\cdot$$
$$\xrightarrow{Br\cdot} Br_3C_2H_3$$

The recovered amount of the polybrominated products is not compatible with a unique way of Br· formation by VB radical scission. Additional amounts of Br· should be formed by the reaction

$$CH_2{=}CH\cdot + HBr \rightarrow CH_2{=}CH_2 + Br\cdot$$

The presence of bromochloroethane in experiments with added HCl could be explained by a similar mechanism.

Additional evidence on the gas-phase disappearance of VB initially formed is provided by energy distribution function calculations (see Appendix 2).

Two models were used. One assumed that all VB formed is found in the gas phase, and in the second case all decomposed diazirine not appearing as acetylene and ethylene was considered to have initially formed VB. The results for pure BMD photolysis (i.e. for the stronger collider) have been plotted in Figure 9 We found similar results using data for the photolysis in (*Z*)-2-butene. It could be observed that while the second model provides input energy distributions similar to those found in the similar photolysis of 3-chloro-3-methyldiazirine,[21] the first only gives an aleatory distribution of points without physical sense.

According to the above discussion the most likely mechanism for the photodecomposition of 3-bromo-3-methyldiazirine can be written as shown in Scheme I.

The experimental acetylene/ethylene ratios deserve some additional comments. These ratios show, except in the experiments with nitrogen, a remarkable lack of pressure dependence (see

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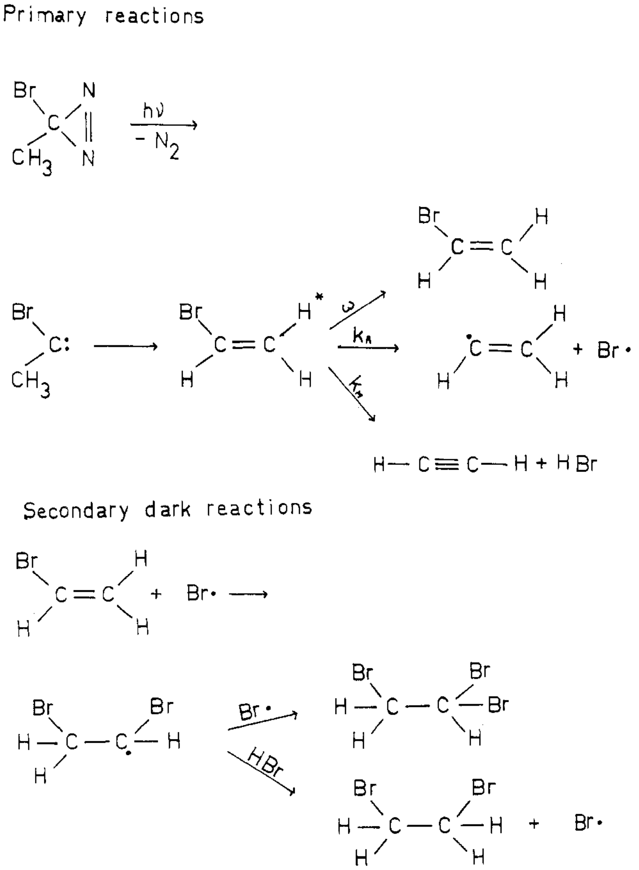
(19) Frisch, M. J.; Pople, J. A.; Binkley, J. S., presented in part at the Annual Congress of the American Chemical Society, Seattle, WA March 1983.

(20) Griller, D.; Liu, M. T. H.; Montgomery, C. R.; Scaiano, J. C.; Wong, P. C. *J. Org. Chem.* **1983**, *48*, 1359.

(21) Figuera, J. M.; Avila, M. J.; Rodrīguez, J. C., manuscript in preparation.

Scheme I. Mechanism for the Photodecomposition of 3-Bromo-3-methyldiazirine



Figures 1–3). Particularly in the photolysis with (*Z*)-2-butene its value stays constant with only low dispersion. In this particular case we can assume that all the vinyl radical formed abstracts hydrogen from the (*Z*)-2-butene. Therefore, we can equal this ratio to the corresponding ratio of the energy-averaged rate constants for each decomposition route:

$$\langle k\rangle_M/\langle k\rangle_R = \text{acetylene/ethylene}$$

where the subscripts M and R identify the molecular and the radical VB decomposition mechanisms, respectively.

In terms of unimolecular theory this ratio can be written within the hard-collision approximation[22] as

$$\langle k\rangle_M/\langle k\rangle_R = \int_{E_0}^{\infty} k(E)_M(\Sigma k)^{-1}f(E)\,dE \Big/ \int_{\epsilon_0}^{\infty} k(E)_R(\Sigma k)^{-1}f(E)\,dE$$

where $k(E)_M$ and $k(E)_R$ are the microscopic rate constant for each process, ω is the collision frequency, Σk is defined as $k(E_M + k(E)_R + \omega$, E is the energy, E_0 is the critical energy for each process, and $f(E)$ is the input energy distribution.

Excluding fortuitous compensation effects, we found only two simple ways of explaining the lack of pressure dependence of the above function.

One is the assumption that the energized VB molecules are formed at a single level of energy E; in this case the equation simplifies to

$$\langle k\rangle_M/\langle k\rangle_R = k(E)_M/k(E)_R$$

where the dependence on ω (i.e. on pressure) disappears, and the ratio of the average rate constants is just the ratio of the microscopic rate constants at the particular energy at which the activated molecules are formed. However, under the assumption mentioned the expression for each individual average rate constant reduces to

$$\langle k\rangle = k(E)\int_{\epsilon_0}^{\infty} f(E)\,dE = k(E)\,N(E) = \text{constant}$$

where $N(E)$ is the total number of activated molecules, all of them formed with the same energy E. This equation indicates a similar lack of pressure dependence in each individual process. Experimental results show that the ratio of the experimental rate constants calculated as $\langle k\rangle = \omega D/S$ at the two extreme limits of higher and lower pressure is 3.6×10^{-2}, far from the expected value of one, thus contradicting the initial assumption made.

The alternative assumption is that within the limits where $f(E) \neq 0$ (i.e. outside of the values that make the integrand equal to zero) the ratio of the two microscopic rates is constant.

The final equation in this case would be

$$k_M/k_R = \langle k\rangle_M/\langle k\rangle_R = k(E)_M/k(E)_R = \text{constant}$$

and the ratio of the microscopic rate constants for the range $f(E) \neq 0$ would be just the experimental D_M/D_R decomposition ratio. According to our experimental data $k_M/k_R = 4.3 \pm 0.4$ for the photolysis in (*Z*)-2-butene.

The expected tendency using the same assumption for photolysis of pure BMD would be a low-pressure acetylene/ethylene limit of about 8, twice the value obtained in the presence of a hydrogen donor (i.e. only vinyl radical disproportionation allowed) and a high-pressure limit close to 4 (i.e. formation of enough of the HBr donor).

The experimental results are compatible with this interpretation (see Figure 2).

The relative higher importance of secondary radical reactions prevents the extension of these ideas to the experiment performed with nitrogen.

Our data also allow the estimation of the energy range where the determined ratio of rate constant holds. According to our calculated effective energy distribution function (see Appendix 2 and Figure 9) for the photolysis with (*Z*)-2-butene, the input energy distribution $f(E)$ is only significantly different from zero in the range 70–90 kcal·mol^{-1}.

Therefore, this is the minimum-energy range where the ratio of microscopic rates should be constant.

Assuming, for the reasons already mentioned (see Appendix 1), that the values of the calculated microscopic rates for the molecular process are reliable, we can calculate the corresponding radical rates using the above experimental ratio for the range 70–90 kcal·mol^{-1}. The results contradict our previous assumption over the radical decomposition mechanism. The model chosen gives much lower rate constants for this energy range (see Figure 7). These discrepancies introduce some uncertainty in the energy distribution calculated from this model. However, this reaction is relatively minor, and the errors thus introduced are of the order of those inherent to the $f(E)$ calculation.

Conclusions

The unexpected participation of a radical path in the photolysis of BMD increases the complexity of the reaction mechanism over those previously reported for other diazirines and makes it difficult to obtain and interpret reliable experimental data.

The partial decomposition of hot VB via a radical path was, as far as we know, discarded as a relevant decomposition way in the previously reported experiments. Our results indicate a molecular to radical decomposition ratio of only 4.3 ± 0.4 under our experimental conditions and also point toward a similar ratio for the corresponding microscopic rates in the 70–90 kcal·mol^{-1} energy range, indicating that the critical energy for the radical decomposition should be closer to that of the molecular process than was previously thought. Additional and more precise experimental and theoretical data are required in order to verify these points.

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(22) Robinson, P. J.; Holbrook, K. A. In "Unimolecular Reactions"; Wiley: London, 1972.

TABLE IV: Frequencies[a] Used in RRKM Calculations of VB Decomposition

molecule[b]	complex molecular path[c]	complex radical path[d]
3014	3014	3014
3076	3076	3076
3100	1801	3100
1605	1106	250
615	631	44
345	pathway c	pathway c
1377	925	1377
1008	1008	1008
1262	1262	1262
497	641	497
902	902	902
940	940	940

[a] In cm^{-1}. [b] From ref 4. [c] Adjusted to available Arrhenius parameters of Cadman and Engelbrech.[4] [d] Estimated from similar reactions.[24]

Work in this direction is in progress.

Acknowledgment. We thank our comrades in the photochemical department for stimulating discussions and CAICYT for its economic support.

Appendix 1. RRKM Calculations of the Microscopic Rate Constants

The vibrational frequency assignment for vinyl bromide has been taken from the literature.[23] Because of the two paths in the unimolecular decomposition of VB, molecular elimination of HBr and radical scission of the C–Br bond, two different activated complexes were assumed.

The activated complexes assignments were chosen under the condition that they should reproduce the Arrhenius preexponential factor (see Table IV).

The values of the A factor ($10^{13.32}$ s^{-1}) and activation energy (64.67 $kcal{\cdot}mol^{-1}$) for the molecular elimination were those given by Cadman,[4a] and the A factor ($10^{14.3}$ s^{-1}) and activation energy (76.74 $kcal{\cdot}mol^{-1}$) for the radical scission were taken from a similar reaction[24] and the heat of formation of the reaction.

The RRKM calculations of the microscopic energy-dependent rate constants, $k_M(E)$ and $k_R(E)$, used the Whitten–Rabinovitch approximations,[25] and the corresponding curves are shown in Figure 7.

Appendix 2. Energy Distribution Function Determination

A mathematical deconvolution method[26] has been used for obtaining the energy distribution function, $f(E)$, of the excited vinyl bromide.

The method requires the knowledge of (a) the unimolecular decomposition data for a set of pressures and (b) unimolecular microscopic rate constants, $k_M(E)$ and $k_R(E)$.

This method is based on the direct mathematical resolution of the equation

$$\frac{D}{D+S}(\omega) = \int_0^\infty \frac{k(E)}{k(E)+\omega} f(E)\,\mathrm{d}E$$

This equation was solved numerically, transforming the integral into a summation with an adequate quadrature.

If we have enough $[D/(D+S)](\omega)$ data, we may write a system of m equations with n unknowns ($m \geq n$) that in matrix representation is reduced to

$$\hat{\mathbf{b}} = \hat{\mathbf{A}}\hat{f}$$

where the elements of $\hat{\mathbf{b}}$ are

$$b_i = \frac{D}{D+S}(\omega_i)$$

The coefficients of the matrix $\hat{A}$ are

$$a_{ij} = \frac{k(E_j)}{k(E_j)+\omega_i}\Delta E$$

and the unknowns of matrix $\hat{f}$ are

$$f_j = f(E_j)$$

By solving the system of linear equations, one can find the values of the energy distribution function.

Registry No. BMD, 4222-23-5; VB, 593-60-2; C_2H_2, 74-86-2; C_2H_4, 74-85-1; HBr, 10035-10-6; SF_6, 2551-62-4; $Br_2HC\text{-}CH_3$, 557-91-5; $Br_3C_2H_3$, 30918-78-6; (*Z*)-butene, 590-18-1; dibromomethane, 74-95-3; 1,2-dibromoethane, 106-93-4.

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(24) Benson, S. W. In "Thermochemical Kinetics"; Wiley: New York, 1968.

(25) (a) Whitten, G. Z.; Rabinovitch, B. S. *J. Chem. Phys.* **1964**, *41*, 1883.

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Correlation Analysis and Linear Solvation Energy Scales: The Implications of Approximate Models

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There are presently a number of empirical single-parameter scales of solvent strength used to correlate solvatochromic phenomena in aprotic liquids. In this work we examine the effects of modeling dipole–dipole and dipole–induced dipole interactions with a single lumped parameter and address the question of whether meaningful information is extractable from linear free energy correlations involving single-parameter scales, for example π^* or E_T. We exclude the possibility of hydrogen-bonding interactions and allow only for general dielectric solvation. In general, we find that, although good to excellent correlation can be obtained, the regression coefficients are often grossly incorrect and not representative of the physical system.

Empirical solvent polarity scales (see ref 1–5 for reviews) serve as a powerful means of organizing the vast literature on studies of solvent effects in areas as diverse as physical organic chemistry and separation science. Further, empirical solvent polarity scales

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(1) Reichardt, C. "Solvent Effects in Organic Chemistry"; Verlag Chemie: Weinheim, West Germany, 1979.

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