

Gas-Phase Negative-Ion Chemistry of Diazomethane

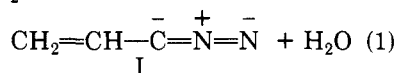
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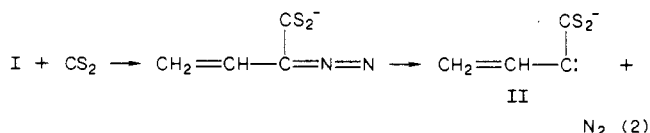
The gas-phase negative-ion chemistry of diazomethane has been investigated by using the flowing afterglow and selected ion flow tube techniques. The gas-phase acidity of diazomethane has been determined to be $\Delta G^\circ_{\text{acid}}(\text{CH}_2\text{N}_2) = 365 \pm 3 \text{ kcal/mol}$ [$\Delta H^\circ_{\text{acid}}(\text{CH}_2\text{N}_2) = 373 \pm 3 \text{ kcal/mol}$] and the electron affinity of the diazomethyl radical has been estimated to be $2.0 \pm 0.3 \text{ eV}$. The reactions of the diazomethyl anion with CS_2 , COS, CO_2 , and SO_2 and with a series of α,β -unsaturated aldehydes and ketones have been studied. Exothermic addition reactions lead to energetic product ions, which fragment by loss of nitrogen. The resulting carbene anions undergo unusual further reactions, either internally or by reaction with the neutral reagents. Michael addition of the diazomethyl anion to the unsaturated aldehydes and ketones can also result in cyclization and loss of an aldehyde to form a pyrazole anion. Diazomethane can also be reduced by hydride transfer to produce an $M + 1$ ion, which is most likely the CH_2NNH^- anion.

Diazoalkanes are among the most reactive of all organic molecules, and their chemistry has been extensively investigated in solution.¹ In the gas phase substituted diazomethyl anions can readily be prepared by reaction of a carbanion with N_2O .² For example the vinyl diazomethyl anion (I) results from the reaction of the allyl anion with N_2O (eq 1). These gas-phase diazomethyl anions



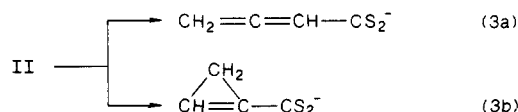
have also proven to be exceedingly reactive, and we have reported on some of their chemistry elsewhere.³ However neither the parent anion, that which arises by proton abstraction from diazomethane itself, nor the corresponding anions from other diazoalkanes have been reported previously in the gas phase. These anions cannot be prepared directly by reactions analogous to that in eq 1 because alkyl anions are too weakly bound with respect to electron detachment for flowing afterglow studies.⁴⁻⁷ We have therefore undertaken a study of the gas-phase ion chemistry of diazomethane and the diazomethyl anion, starting with the neutral precursor itself. In particular, we have determined the gas-phase acidity of diazomethane, estimated the electron affinity of the corresponding diazomethyl radical, and explored the addition-fragmentation pathways that the diazomethyl anion undergoes with a number of neutral molecules.

In our earlier work³ we found that when a substituted diazomethyl anion undergoes a highly exothermic addition reaction, the resulting anion fragments by loss of nitrogen because it is unable to transfer its energy to solvent (eq 2). However the ionic product is very unreactive and does

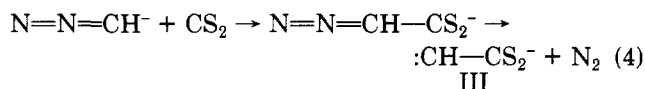


not appear to have a carbene structure, as for example II, which would be expected as the initial product of loss of nitrogen. We therefore proposed³ that II rearranges, either

to an allene (eq 3a) or a cyclopropene (eq 3b). However we were unable to determine which, if either, of these structures is correct.



If the diazomethyl anion reacts analogously with CS_2 and other electrophiles, a carbene anion (III) could form (eq 4), which, because of the lack of a vinyl substituent, would be unable to rearrange by the pathways of eq 3. We hoped



that we would be able to study the gas-phase chemistry of such a species, or determine if it too rearranges to a more stable isomer. In addition, we were interested in studying the gas-phase ion chemistry of the neutral diazoalkane and in determining the acidity of diazomethane and the electron affinity of the corresponding diazomethyl radical.

Experimental Section

The experiments described in this paper were carried out with a flowing afterglow apparatus (FA)⁸ and a tandem flowing afterglow-selected ion flow tube (FA-SIFT),⁹ both of which have been described previously. Briefly, ions (HO^- , NH_2^- , F^-) are prepared by electron impact on appropriate precursors in a stream of helium (8000 cm/s, 0.4 Torr) confined in a 1-m long \times 7.6-cm i.d. stainless steel tube. After being thermally equilibrated by many collisions with the helium bath gas and precursor gases, the ions are allowed to react with diazomethane, whose vapors enter the flow tube downstream from the ionizing region. The diazomethyl anion is formed by proton transfer. In the FA, reagent gases are added at various ports further along the flow

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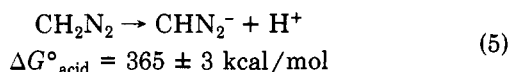
tube and allowed to react with the diazomethyl anion. At the end of the flow tube the plasma is sampled through a 0.5-mm orifice into a low-pressure region where the ions are separated in a quadrupole mass filter and detected by an electron multiplier. In the FA-SIFT the ion of interest (e.g. CHN_2^-) is produced in the first flow tube by allowing diazomethane to react with hydroxide ion, mass-selected in the first quadrupole and injected into a second flow tube where its chemistry is investigated in the absence of ions of other masses, neutral precursors, photons, and electrons. At the end of the second flow tube product ions are again sampled and analyzed in a quadrupole.

Diazomethane was prepared from *N*-nitrosomethylurea by reaction with base according to the method given in *Organic Syntheses*.¹⁰ For our first experiments the ether layer was omitted and instead helium was passed over the surface of the reaction mixture, and pure diazomethane was swept into a liquid nitrogen trap, where it crystallized. The trap was then connected to an inlet of the FA, and diazomethane (bp 250 K) was allowed to distill into the flow tube. In later experiments the ether layer was replaced by decalin, which was separated from the mixture and placed in a flask after the reaction was complete. The flask was then attached to an inlet of the flow tube, and diazomethane was again allowed to distill, this time directly from the decalin solution. Both methods afforded intense signals of the diazomethyl anion as essentially the only ion formed upon reaction with HO^- or other strongly basic anions.

The gases used in this study were of the following purity: He (99.995%), NH_3 (99.995%), N_2O (99.99%), CH_4 (99.97%). Other compounds were of reagent grade obtained commercially and were used without further purification.

Results and Discussion

Diazomethane is quite acidic and reacts with strong bases exclusively by proton abstraction. Its gas-phase acidity, which is defined as the free energy of its ionization to the diazomethyl anion and a proton (eq 5), was determined by the bracketing technique. In this technique



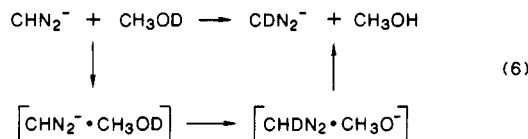
diazomethane is allowed to react with a series of bases, A^- , of known basicity and the occurrence or nonoccurrence of proton transfer is monitored. If complete proton transfer is observed, then diazomethane is a stronger acid than AH. The lack of proton transfer suggests but does not prove that diazomethane is a weaker acid than AH since there may be a kinetic barrier preventing reaction on the FA timescale. To test for this possibility, we carried out bracketing in the opposite direction, starting from the diazomethyl anion and allowing it to react with a series of acids, AH. In this case the observation of proton transfer demonstrates that diazomethane is a weaker acid than AH. We also investigated the kinetic mobility of proton-transfer reactions by studies of hydrogen-deuterium exchange reactions (see below).

We found that diazomethane reacts rapidly by proton transfer with NH_2^- ($\Delta G^\circ_{\text{acid}}(\text{NH}_3) = 396.1 \pm 0.7 \text{ kcal/mol}$),¹¹ HO^- ($\Delta G^\circ_{\text{acid}}(\text{H}_2\text{O}) = 384.1 \pm 0.4 \text{ kcal/mol}$),¹¹ and HO_2^- ($\Delta G^\circ_{\text{acid}}(\text{H}_2\text{O}_2) = 369.1 \pm 0.6 \text{ kcal/mol}$).¹² It reacts slowly with F^- ($\Delta G^\circ_{\text{acid}}(\text{HF}) = 365.7 \pm 0.5 \text{ kcal/mol}$),¹¹ but even at high diazomethane flows some F^- remains; this indicates that diazomethane and HF are close in acidity. When diazomethane is allowed to react with acetone enolate ion ($\Delta G^\circ_{\text{acid}}(\text{acetone}) = 361.9 \pm 2.0 \text{ kcal/mol}$),¹¹

only a trace of the diazomethyl anion is observed. Therefore the acidity of diazomethane appears to lie between that of H_2O_2 and acetone, $369 > \text{CH}_2\text{N}_2 > 362$.

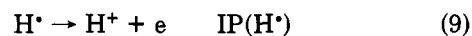
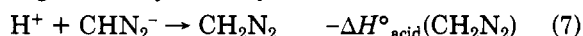
We next examined the reverse reaction, that of the diazomethyl anion with acids. It does not abstract a proton from methyl isonitrile ($\Delta G^\circ_{\text{acid}} = 366 \pm 3 \text{ kcal/mol}$)¹³ but does so slowly from acetonitrile ($\Delta G^\circ_{\text{acid}} = 365.2 \pm 2.0 \text{ kcal/mol}$).¹¹ Proton transfer was observed from acetone ($\Delta G^\circ_{\text{acid}} = 361.9 \pm 2.0 \text{ kcal/mol}$)¹¹ but not from NH_3 , H_2O , or CH_3OH .

To obtain an estimate of the kinetic mobility of the protons in diazomethane we examined hydrogen-deuterium exchange reactions of CHN_2^- . Thus, although no methoxide ion is formed when the diazomethyl anion reacts with CH_3OH , ready exchange occurs with CH_3OD (eq 6). In such exchange, which we have discussed in detail



elsewhere,¹⁴ endothermic proton and/or deuteron transfers occur within an ion-dipole complex. The observation of such exchange in the absence of formation of methoxide ion shows that there is a thermodynamic but not a kinetic barrier to proton transfer. The energy for these transfers comes from the ion-dipole and ion-induced dipole attractions between the ion and the neutral reagent and is typically in the range of 10–20 kcal/mol. No exchange is observed upon reaction of CHN_2^- with D_2O , indicating that the endothermicity of deuteron transfer must be greater than the complexation energy for this reagent. Taking all of these results together, we assign $\Delta G^\circ_{\text{acid}}(\text{CH}_2\text{N}_2) = 365 \pm 3 \text{ kcal/mol}$. Use of an estimate of $\Delta S^\circ_{\text{acid}}(\text{CH}_2\text{N}_2) = 27 \text{ eu}$,¹⁵ due mainly to the entropy of the proton, gives $\Delta H^\circ_{\text{acid}}(\text{CH}_2\text{N}_2) = 373 \pm 3 \text{ kcal/mol}$ at 300 K.

The electron affinity (EA) of the diazomethyl radical, N_2CH^* is related to the gas-phase acidity of diazomethane, its carbon-hydrogen bond dissociation energy (BDE), and the ionization potential (IP) of the hydrogen atom by the following thermodynamic cycle.



Two of these values, $\Delta H^\circ_{\text{acid}}$ and $\text{IP}(\text{H}^*)$ (313.6 kcal/mol),¹⁶ are known. The bond dissociation energy of diazomethane is not known. However the carbon-hydrogen BDE of the isoelectronic molecule ketene, CH_2CO , has recently been found to be $105.9 \pm 2.1 \text{ kcal/mol}$,¹⁷ and this would seem to be a good model for diazomethane. If we assume ketene and diazomethane to have a similar C–H BDE, we can estimate the electron affinity of the diazomethyl radical to be about 46 kcal/mol ($2.0 \pm 0.3 \text{ eV}$), somewhat less than that of the ketylenyl radical (2.35 eV).¹⁷

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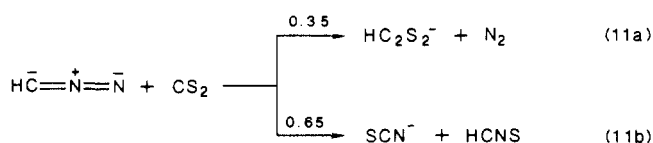
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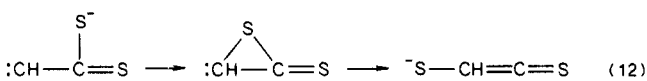
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Reaction of the diazomethyl anion with CS₂ occurs rapidly to form two ionic products,¹⁸ an ion HC₂S₂⁻ corresponding to addition and loss of nitrogen (eq 11a) and the thiocyanate ion, SCN⁻ (11b). We postulate that the

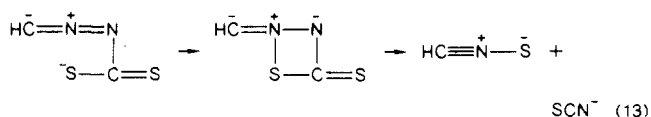


former ion arises by addition and fragmentation to form initially a carbene; however, the product ion is quite unreactive and shows no chemical reactions characteristic of a carbene, in great contrast to the chemistry of the analogous ion formed by reaction with CO₂ (see below). We therefore believe that the initially formed carbene rearranges to a more stable structure. Since in this case there is no vinyl substituent, one of the sulfur atoms must interact with the carbene to form either a stable cyclic compound or, by subsequent ring opening, a thio ketene derivative (eq 12). It is certainly conceivable that a similar

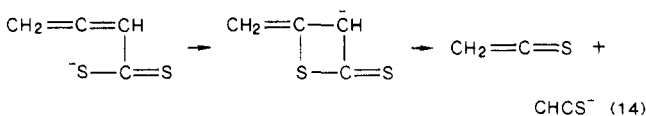


rearrangement takes place when CS₂ reacts with I, and analogous product ions should be added to those of eq 3. We have been unable to discover any characteristic reactions of these ions that would serve to identify their structure(s). Conceivably collision-induced dissociation reactions might serve to distinguish among the possibilities.¹⁹

Note that the major product (65%) of the reaction of the diazomethyl anion with CS₂ is the thiocyanate ion; this ion is formed in only trace amounts from the reaction of I³. Diazomethyl anions are ambident, and reaction can, in theory, occur on either the carbon or the terminal nitrogen. We formulate the thiocyanate ion to arise from the latter attack, as shown in eq 13. The diazomethyl



anion is isoelectronic with the allenyl anion, which can readily be prepared in the gas phase by proton abstraction from allene with HO⁻. In our earlier paper³ we noted that the allenyl anion reacts with CS₂ to give a cleavage reaction (eq 14), which is completely analogous to that of eq 13.

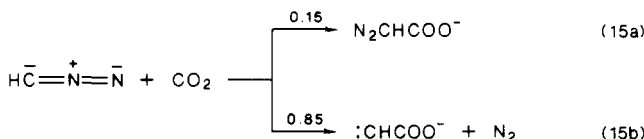


The much greater amount of SCN⁻ formed from the diazomethyl anion as compared to the vinyl diazomethyl anion most likely reflects a greater amount of negative charge on nitrogen in the former ion, since the charge is less delocalized. However we cannot rule out the possibility that addition of CS₂ within the ion-dipole complex is reversible and that the ratio of the two products formed reflects the relative rates of the subsequent fragmentation reactions.

(18) Throughout this paper, indicated branching ratios are estimates only; no corrections have been made for mass discrimination.

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Reaction of the diazomethyl anion with CO₂ leads to the formation of an adduct and an adduct that has lost nitrogen (eq 15). The latter ion is, in contrast to the cor-



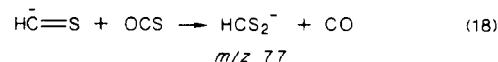
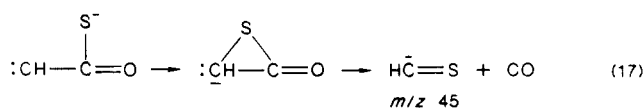
responding ion from CS₂, highly reactive and quickly picks up an additional oxygen from another molecule of CO₂ to form an unreactive ion, which we formulate as the glyoxylate ion (eq 16). There is obviously a great difference



in reactivity between the product ions formed by addition of CO₂ and loss of N₂ and those formed by addition of CS₂ and loss of N₂. The ions from reaction with CO₂ appear to behave like carbenes while those from reaction with CS₂ do not.

We note as well a second difference in the two reactions. Reaction with CS₂ leads to the formation of SCN⁻ without formation of an adduct, while an adduct and no OCN⁻ is formed upon reaction with CO₂. This observation is fully consistent with our earlier studies of the allenyl anion.³ Reaction with CS₂ produces the thio ketene anion as we have noted (eq 14) and no adduct, while reaction with CO₂ gives only adduct and no ketene anion. Additions to CO₂ are less exothermic than those to CS₂,³ and therefore there is less energy in the adduct to induce fragmentations and rearrangements.

Reaction of the diazomethyl anion with OCS resembles that with CS₂ in that SCN⁻ (branching ratio = 0.15) and an unreactive adduct that has lost N₂ (0.35)²⁰ are important products. In addition a new primary product ion of *m/z* 45 is produced (0.50) and this ion reacts further with OCS to produce an ion of *m/z* 77. On the basis of the intensities of the *M* + 2 peaks the *m/z* 45 ion contains one and the *m/z* 77 ion contains two sulfur atoms, and therefore their structures must be HCS⁻ and HCS₂⁻, respectively. The former ion could arise from a cyclic ion like that postulated earlier (eq 12) by loss of carbon monoxide (eq 17). The



resulting thioformyl anion would be expected to abstract a sulfur atom from OCS since other acyl anions react in this way.²¹ The reaction of eq 17 would be more favorable than the corresponding one from CS₂ since loss of CO is much more exothermic than loss of CS. Indeed sulfur abstraction reactions like that of eq 18 occur much more readily with OCS (to form CO) than they do with CS₂ (to form CS).²²

The reactivity of the diazomethyl anion with CS₂, OCS, and CO₂ is consistent with that observed for substituted

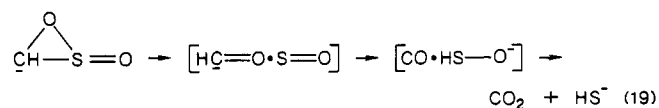
(20) This *m/z* 73 ion could also correspond to the sulfur transfer product CHN₂S⁻; however, the identification as ⁻SCHCO, corresponding to addition with loss of N₂, is consistent with the mechanism outlined for the reaction with CS₂ (eq 12).

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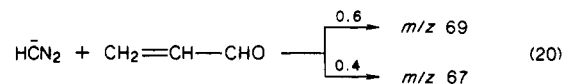
derivatives, where the major reaction pathways are addition and addition with fragmentation. We noted earlier that as the reaction exothermicity increases, more fragmentation of the initially formed adduct occurs.³ The same trend is seen with the parent anion. The least exothermic addition, that of CO₂, results in the least fragmentation, and some of the simple adduct, without fragmentation, is observed as a product. Simple adducts are not observed in the more exothermic reactions with OCS and CS₂. We also note that reactions with the diazomethyl anion lead to more extensive fragmentation than do those of substituted diazoanions. This is consistent with the greater number of degrees of freedom in the latter ions, which are thus better able to accommodate the reaction exothermicity internally, giving them a longer lifetime and an increased probability for collisional stabilization. Furthermore, the substituted diazoanions are less basic so that the overall reaction exothermicity is decreased. There also seems to be a much greater propensity for the parent ion to react at the nitrogen atom than in the case with the substituted derivatives. With the substituted vinyl diazomethyl anions minor products corresponding to nitrogen substitution were observed with CS₂. In contrast, with the parent diazomethyl anion, major amounts of nitrogen substitution products (S=C=N⁻) were observed with CS₂ and, in addition, moderate amounts were observed with COS.

Reaction of the diazomethyl anion with SO₂ should be even more exothermic, and indeed three fragmentation product ions are formed in this reaction. The major channel is addition followed by loss of nitrogen to form an unreactive ion (branching ratio = 0.50), as was the case with the other reactants, but two other major pathways are also observed, one to form HSO⁻ (0.25) and the other to form HS⁻ (0.25). These reduced sulfur species are indeed reaction products and are not due to impurities in the SO₂ since they are not produced upon reaction of the same SO₂ sample with other ions. We believe that these ions can be accounted for in terms of the general mechanism we have postulated for other reactions of the diazomethyl anion. Addition of SO₂ and loss of nitrogen will give rise to a carbene, which can ring-close and, as shown in eq 19, lose SO with the formation of the formyl anion, in analogy with formation of CO and the thioformyl anion above (eq 17). Since the formyl anion is such a strong

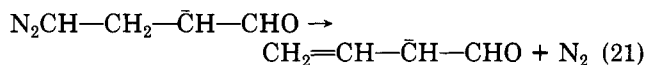


hydride donor,²³ it can reduce the SO. The resulting HSO⁻ can either escape from the complex or oxidize the CO to CO₂, forming HS⁻. We have noted in a previous publication²⁴ that HOO⁻ will oxidize CO to CO₂. Although the reduction of SO₂ to HS⁻ is certainly striking, it should be noted that the overall reaction from the diazo anion and SO₂ to HS⁻, N₂ and CO₂ is exothermic by approximately 120 kcal/mol.

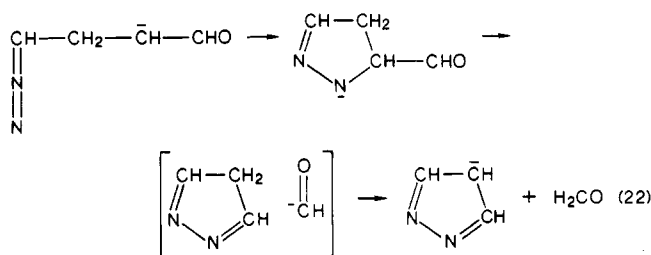
With most organic compounds the diazomethyl anion is either unreactive or undergoes proton transfer. However, with acrolein it produces two ionic products as shown in eq 20. To deduce the empirical formulas of these ions we first used ¹⁸O as a label. This was simply done by adding a drop of H₂¹⁸O and a trace of acid to the flask containing



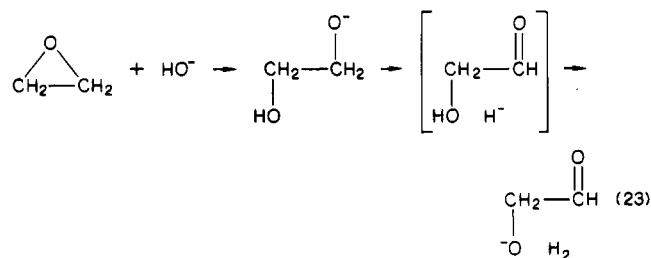
the acrolein. Gradual incorporation of the label into the aldehyde could be monitored by allowing it to react with HO⁻ and examining the M - 1 ion. At the same rate the label was introduced into this latter ion, it appeared in the *m/z* 69 product ion. We therefore formulate this ion as a Michael adduct that has lost N₂. Since it is an unreactive ion, we assume that the initially formed carbene rearranges to an olefin (eq 21).



The *m/z* 67 ion, however, does not incorporate the ¹⁸O label and therefore must have the formula C₃H₃N₂⁻ and result from addition and loss of formaldehyde. The two most reasonable structures for an ion of this formula are the vinyl diazomethyl anion (I) and the anion formed by proton abstraction from pyrazole. We prepared the latter ion by allowing pyrazole to react with HO⁻. When CS₂ was added an adduct forms from which little or no loss of nitrogen was observed. This is in sharp contrast to the reaction of I with CS₂ (eq 2). We therefore carried out the reaction between the diazomethyl anion and acrolein in our SIFT, injected the *m/z* 67 ion into the second flow tube, and allowed it to react with CS₂. We repeated the experiment with authentic I and with the M - 1 ion of pyrazole. In its reaction with CS₂ the *m/z* 67 ion produced by the reaction of eq 20 was identical with the ion from pyrazole. We postulate that it is formed from the Michael adduct by the sequence shown in eq 22. The loss of the



formyl anion within the ion-dipole complex would undoubtedly be an endothermic process from the ground-state ion. However, the ion contains the reaction exothermicity of the addition and cyclization so that an endothermic reaction can proceed. Another example of a reaction that proceeds through the intermediate elimination of a strongly basic anion is shown in eq 23.²⁵



As further confirmation of both the structure of the product ion and of the mechanism proposed in eq 22, we prepared the deuteriodiazomethyl anion by allowing the diazomethyl anion to react with CH₃OD in the first flow tube (eq 6), injecting the *m/z* 42 ion, and allowing it to

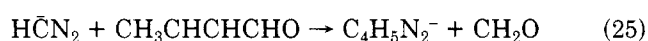
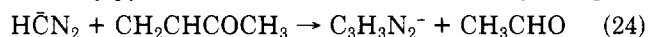
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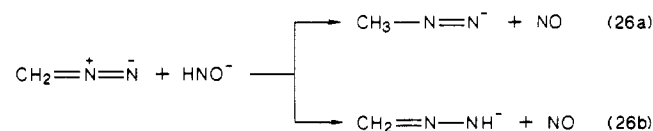
react with acrolein. As expected for the series of reactions shown in eq 22, the product ion was m/z 68, corresponding to the incorporation of a deuterium atom. If the product had been I, no deuterium incorporation would be expected.

Other α,β -unsaturated carbonyl compounds react analogously. Addition to methyl vinyl ketone results in loss of acetaldehyde and again the formation of pyrazole anion (eq 24) while crotonaldehyde forms a small amount of methylpyrazole anion with loss of formaldehyde (eq 25).



Similarly, methacrolein forms methylpyrazole anion and tiglic aldehyde (*trans*-2-methyl-2-butenal) forms a small amount of dimethylpyrazole anion with loss of formaldehyde. For these carbonyl compounds, proton abstraction and addition with loss of N_2 are important, often major, channels. On the other hand, mesityl oxide ($(\text{C}-\text{H}_3)_2\text{CCHCOCH}_3$) fails to react with the diazomethyl anion, either because the presence of the two β -methyl groups blocks Michael addition or because there is no acidic proton to abstract from the cyclization product.

As a neutral reagent diazomethane undergoes few gas-phase ionic reactions other than proton abstraction. We did find, however, that it accepts a hydride ion from HNO^- .²⁴ In theory, addition could occur at either carbon (eq 26a) or at nitrogen (eq 26b).



form an azomethyl anion, which might be expected to lose nitrogen easily;²⁶ the product ion formed is quite stable and unreactive and is best formulated as the anion from formaldehyde hydrazone (eq 26b). This is in accord with the usual site of reaction of diazo compounds with reducing agents in solution.¹

In summary, we have found that the diazomethyl anion reacts in interesting ways with a number of reagents in the gas phase. An initially exothermic addition reaction can deposit sufficient energy into the product ion to induce loss of nitrogen to form a carbene, which in turn may rearrange, fragment further, or react with a neutral reagent. Michael adducts are also found to cyclize and eliminate aldehydes to form pyrazole anions as well as to lose nitrogen. Diazomethane itself undergoes a proton transfer reaction with most ionic reagents but can be reduced by an appropriate hydride donor.

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Registry No. CH_2N_2 , 334-88-3; CHN_2^+ , 20813-32-5; CHN_2^- , 100840-43-5; CS_2 , 75-15-0; COS , 463-58-1; CO_2 , 124-38-9; SO_2 , 7446-09-5; CH_3OH , 67-56-1; $\text{CH}_2=\text{CHCHO}$, 78-94-4; $\text{CH}_2=\text{CHCOCH}_3$, 78-94-4; $\text{CH}_3\text{CH}=\text{CHCHO}$, 4170-30-3; pyrazole, 288-13-1; methacrolein, 78-85-3; tiglic aldehyde, 497-03-0.

(26) The dissociation of CH_3N_2^- to methide ion and molecular nitrogen is expected to be exothermic as long as the hydride affinity of CH_2N_2 to form CH_3N_2^- is ≤ 70 kcal/mol. Based on known hydride affinities of other molecules, this upper limit appears reasonable.

Investigation on Factors Ruling Catalytic Efficiency and Chemical Stability of Mn(III) Porphyrins in HOCl Olefin Epoxidation: Conditions for Practical Application

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The use of stable Mn(III) porphyrins (P), e.g. 2-4, and of imidazole or pyridine axial ligands (L), 8-10, entirely soluble in the organic phase has allowed an extensive investigation of the factors ruling the catalytic activity of porphyrins in the olefin epoxidation carried out at 0 °C under two-phase conditions with ClO^- and/or HOCl as oxidants. We have determined (i) the influence of the pH of the aqueous phase and of the phase-transfer catalyst on the reaction rate and on the Mn(III) porphyrins stability; (ii) the best ligand/porphyrin ratio (L/P) necessary to obtain the fastest conversion of cyclooctene (more reactive substrate) and 1-dodecene (less reactive substrate) to the corresponding epoxides; (iii) the oxidative demolition of the axial ligands 8-10; (iv) the activity of *N*-oxides 11 and 12 as axial ligands; (v) the possibility to epoxidize reactive olefins with HOCl in the absence of the phase-transfer catalyst and of the axial ligand, buffering the pH of aqueous NaOCl at 10.5. The association constants (K_1 , K_2) of imidazole with Mn(III) porphyrins 1 and 2 and of *N*-hexylimidazole (8) with 2 have also been evaluated in order to rationalize the effect of ligand/porphyrin ratio on the reaction rate.

Mn(III) tetraarylporphyrins have been used by Tabushi,¹ Meunier,² Collman,³ and others^{4,5} as catalysts in olefin

epoxidation promoted by NaOCl under phase-transfer conditions.⁶ Reaction rates are greatly enhanced when

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