# Dichlorocarbene

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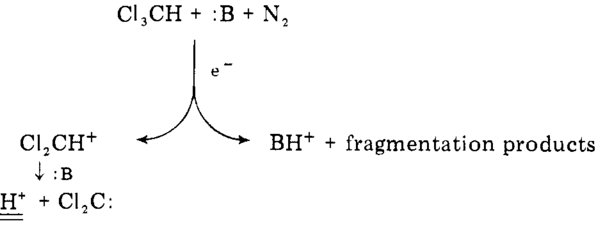
**Abstract:** The enthalpy of deprotonation of the dichloromethyl cation, generated by electron impact in an ion cyclotron resonance spectrometer from $CHCl_3$, has been determined to be 208.3 ± 2 kcal/mol. This value, combined with $\Delta H_f°$ (298 K) for $Cl_2CH^+$ (212 kcal/mol), leads to a heat of formation for dichlorocarbene of 53.1 ± 2 kcal/mol. Additionally, the enthalpy of deuteron abstraction from deuteriodichloromethyl cation (generated from deuteriochloroform) has been measured as 209.0 ± 2 kcal/mol, leading to a heat of formation of dichlorocarbene of 53.8 ± 2 kcal/mol.

## Introduction

Species such as dichlorocarbene, members of the class of divalent carbon compounds believed to possess singlet electronic ground states, have long been established as short-lived intermediates in a variety of organic reaction processes.[1] It is somewhat surprising, therefore, that fundamental physical structure and energy data on such compounds are scarce, in fact, all but lacking on any but the simplest members in the series. Although the infrared spectra of a few substituted carbenes,[2] including the dichloro compound,[3] have now been obtained, enabling details of their geometrical structures to be discerned, very little progress has been made toward the experimental determination of the relative thermochemical stabilities of such molecules. The only singlet carbenes for which reliable thermochemical data appear to be available are the difluoro- and dichloro-substituted compounds.[4]

We describe in this paper a simple and general experimental procedure which enables the determination of the heat of formation of singlet carbenes, :CXY.[5] It is outlined in Scheme I for the particular case of dichlorocarbene. Electron impact on a mixture of an inert buffer gas (in our case, $N_2$), chloroform, and a base B of known strength contained in an ion cyclotron resonance spectrometer[6] leads primarily to the formation of the dichloromethyl cation, and (depending on the nature of the reference base) to small quantities of $BH^+$ and to fragmentation products of B. If B is a sufficiently strong base, it will abstract a proton from the dichloromethyl cation, resulting in the production of an ion of mass corresponding to $BH^+$, and the formation, at least transiently, of the neutral species, dichlorocarbene. All that needs to be done, therefore, is to determine the weakest base within a series of standards which is capable of abstracting a proton from $Cl_2CH^+$, or, equivalently, the strongest reference compound which is not capable of proton abstraction. The enthalpy of protonation of this particular base, combined with the known heat of formation of $Cl_2CH^+$, leads directly to a value for $\Delta H_f°$ for dichlorocarbene. As mentioned previously, an ion of mass corresponding to $BH^+$ might possibly arise from self-protonation of B, following initial electron impact, as well as from deprotonation of the dichloromethyl cation. Double resonance techniques have, therefore, been employed to ensure that $BH^+$ derives at least in part, if not wholly, from the latter route.

Scheme I



We have also studied the thermochemistry of deuteron abstraction from $CDCl_2^+$ as derived from deuteriochloroform. This provides us with an independent determination of $\Delta H_f°$ for dichlorocarbene.

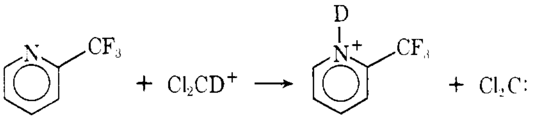
## Results and Discussion

Our experimental data are displayed in Table I. Aniline (free energy of proton transfer, 6.7 kcal/mol greater than that for ammonia) is the strongest base examined for which proton abstraction from $Cl_2CH^+$ was not observed; 3,3,3-trifluoro-1-propylamine (free energy of proton transfer, 6.9 kcal/mol greater than that for ammonia) is the weakest base for which proton transfer was established. We conclude that the free energy change for the reaction

$$CF_3CH_2CH_2NH_2 + Cl_2CH^+ \rightarrow CF_3CH_2CH_2NH_3^+ + Cl_2C:$$

is 0 ± 2 kcal/mol[7] (enthalpy of proton transfer of −0.7 ± 2 kcal/mol[8]) and that the enthalpy of protonation of dichlorocarbene is 208.3 ± 2 kcal/mol.[8,9] Combined with the heat of formation of $Cl_2CH^+$ (212 kcal/mol),[10] this value leads to $\Delta H_f°$ (298 K) for dichlorocarbene of 53.1 ± 2 kcal/mol.

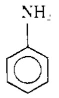
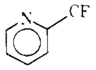
3,3,3-Trifluoro-1-propylamine was not observed to abstract a deuteron from the deuteriodichloromethyl cation. Rather, a stronger base, 2-(trifluoromethyl)pyridine (free energy of proton transfer, 7.5 kcal/mol greater than that for ammonia), was required. Here we conclude that both the free energy and enthalpy changes for the reaction



are 0 ± 2 kcal/mol, corresponding to an enthalpy of deuterium transfer to dichlorocarbene of 209.0 ± 2 kcal/mol. Ignoring small differences due to secondary isotope effects, this value leads to a heat of formation of $Cl_2C$: of 53.8 ± 2 kcal/mol, in good agreement with our determination using the unlabeled compound.

The heat of formation of dichlorocarbene has been the subject of two recent experimental studies. Benson and Spokes have proposed a value of 53 kcal/mol for $\Delta H_f°$ (298 K) of dichlorocarbene,[11] arrived at by their determination of the activation energy required for elimination of HCl by chloroform, assuming a $\Delta E^{\ddagger}$ of zero for the reverse process. Shapiro and Lossing have employed their measured appearance potentials for $CCl_2^+$ from each of chloroform and tetrachloroethylene to arrive at a slightly higher value of 56.5 ± 5 kcal/mol for $\Delta H_f°$ (298 K) of $:CCl_2$.[12] The fact that our data for dichlorocarbene is in good accord with these previous determinations lends credence to the ICR technique, and suggests its value in the elucidation of the thermochemical stabilities

Table I. Observation of ICR Spectroscopy of Proton Abstraction from Dichloromethyl Cation and Deuteron Abstraction from Deuteriodichloromethyl Cation

| Abstracting base, B | Free energy of protonation of B, kcal/mol[a] | Does B abstract a proton from $Cl_2CH^+$? | Does B abstract a deuteron from $Cl_2CD^+$? |
|---|---|---|---|
| $(i\text{-Pr})_2O$ | 1.9 | No | |
| $(i\text{-Pr})_2S$ | 5.8 | No | No |
|  | 6.7 | No | — |
| $CF_3CH_2CH_2NH_2$ | 6.9 | Yes | No |
|  | 7.5 | Yes | Yes |
| $MeNH_2$ | 9.2 | Yes | Yes |

[a] Relate to ammonia. Except for $(i\text{-Pr})_2S$ experimental data from R. W. Taft in "Proton Transfer Reactions", E. F. Caldin and V. Gold, Ed., Wiley-Halsted, New York, N.Y., 1975, p 31, with small corrections based on additional unpublished results of J. F. Wolf and J. L. M. Abboud.

of other substituted carbenes. Research in this direction is in progress.

## Experimental Section

All studies were performed on a trapped cell ion cyclotron resonance spectrometer described previously.[6] Electron energies were on the order of 15 eV for $CHCl_3$ and 12 eV for $CDCl_3$. Total neutral pressures for the experiments involving $CHCl_3$ were on the order of $1 \times 10^{-5}$ Torr and for the $CDCl_3$, $3 \times 10^{-6}$ Torr. For the $CHCl_3$ studies conducted in the presence of a buffer gas ($N_2$), the neutral pressure ratios were approximately 1:10:100 (base:$CHCl_3$:buffer). For the $CDCl_3$ studies, conducted in the absence of buffer gas, the neutral pressure ratios were 1:1-3 (base:$CDCl_3$).

During the double resonance experiment the intensity of the signal corresponding to $BH^+$ (or $BD^+$) is observed while the cell is irradiated with an rf pulse having a frequency corresponding to the cyclotron frequency of $CHCl_2$+ (or $CDCl_2^+$). The peak-to-peak rf level of the pulse is 0.5 V, sufficient to eject the entire population of $CHCl_2^+$ (or $CDCl_2^+$) from the cell within a few milliseconds. If the intensity of $BH^+$ (or $BD^+$) is observed to decrease upon application of the pulse then we infer that the $CHCl_2^+$ (or $CDCl_2^+$) is a source of protons (or deuterons) for the base. If the base derives only part of its protons (or deuterons) from $CHCl_2^+$ ($CDCl_2^+$) then the intensity of $BH^+$ (or $BD^+$) is not seen to decrease to zero.

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## References and Notes

(1) For recent reviews see (a) W. Kirmse, "Carbene Chemistry", 2nd ed, Academic Press, New York, N.Y., 1971; (b) M. Jones, Jr., and R. A. Moss, Ed., "Carbenes", Wiley-Interscience, New York, N.Y., Vol. 1, 1973, Vol. 2, 1975.
(2) For a tabulation of recent results, see A. J. Downs and S. C. Peak, *Mol. Spectrosc.* **1** (1973); **3** (1965).
(3) (a) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **47**, 703 (1967); (b) L. Andres, *ibid.*, **48**, 979 (1968); (c) M. E. Jacox and D. E. Milligan, *ibid.*, **53**, 2688 (1970); (d) A. K. Maltsev, R. G. Mikaelyan, and O. M. Nefedou, *Bull. Acad. Sci. USSR*, 188 (1971).
(4) For a summary of available thermochemical data see D. R. Stull and H. Prophet, "JANAF Thermochemical Tables", 2nd ed, NSRDS-NBS 37, National Bureau of Standards, Washington, D.C., 1971.
(5) For examples of the use of similar techniques in the elucidation of the thermodynamic stabilities of transient ions and neutral species see (a) ions, D. J. DeFrees, R. T. McIver, Jr., and W. J. Hehre, *J. Am. Chem. Soc.*, **99**, 3853 (1977); (b) free radicals, D. J. DeFrees, W. J. Hehre, R. T. McIver, Jr., and D. H. McDaniel, *ibid.*, submitted; (c) enol forms of stable ketones, S. K. Pollack and W. J. Hehre, *ibid.*, **99**, 4845 (1977); (d) methylenimine, D. J. DeFrees and W. J. Hehre, *J. Phys. Chem.*, submitted. (e) A similar approach has been employed by Beauchamp in the determination of the heat of formation of $CF_2$: J. Vogt and J. L. Beauchamp, *ibid.*, **97**, 6682 (1975).
(6) For descriptions of pulsed ion cyclotron resonance spectroscopy, see (a) R. T. McIver, Jr., *Rev. Sci. Instrum.*, **41**, 555 (1970); (b) J. D. Baldeschwieler and S. S. Woodgate, *Acc. Chem. Res.*, **4**, 114 (1971); (c) R. T. McIver, Jr., and R. C. Dunbar, *Int. J. Mass Spectrom. Ion Phys.*, 7, 471 (1971).
(7) Several sources of error contribute to the quoted 2 kcal/mol uncertainty. These are (a) need for the assignment of an absolute for the proton affinity scale (see ref 9), (b) the finite resolution of the proton affinity scale, and (c) the likelihood that slightly endothermic proton transfer reactions as well as thermoneutral and exothermic processes will occur. We suspect that the quoted error limit is large enough to take account of these factors.
(8) We assume that $\Delta S$ may be ascribed to symmetry number changes only. For a discussion, see S. W. Benson, "Thermochemical Kinetics", 2nd ed, Wiley-Interscience, New York, N.Y., 1976, pp 47-50.
(9) Based on an absolute proton affinity for ammonia of 202.3 kcal/mol. Such a value has been selected in order that the proton affinity scales independently obtained by high-pressure mass spectrometry [R. Yamadagni and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 1320 (1976)] and ion cyclotron resonance spectroscopy [J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, J. L. Beauchamp, R. T. McIver, Jr., and R. W. Taft, *ibid.*, **99**, 5417 (1977)] best match previous measurements on a selected number of reference compounds.
(10) F. P. Lossing, *Bull. Soc. Chim. Belg.*, **81**, 125 (1972).
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(12) J. S. Shapiro and F. P. Lossing, *J. Phys. Chem.*, **72**, 1552 (1968).