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Benzylchlorocarbene: Origins of Arrhenius Curvature in the Kinetics of the 1,2-H Shift Rearrangement

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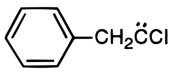
Benzylchlorocarbene (**1**, BCC) was generated photochemically from benzylchlorodiazirine (**2**) in isooctane, methylcyclohexane (MCH), and tetrachloroethane (TCE) at temperatures from ~30 to −75 °C. At −70 °C in isooctane, the identified products included Z/E-β-chlorostyrenes **4** (46.6%), α-chlorostyrene **5** (2.4%), 1,1-dichloro-2-phenylethane **6** (1.9%), a BCC-isooctane insertion product **8** (5.5%), carbene dimers **9** (3.8%), and azine **3** (30%). The significant incursion of intermolecular products **3**, **8**, and **9** implies that laser flash photolytic (LFP) kinetic data for the decay of BCC obtained at low temperature is biased and should not be employed in Arrhenius analyses. Accordingly, previously obtained curved Arrhenius correlations for BCC do not necessarily implicate quantum mechanical tunneling (QMT) in the 1,2-H shift rearrangement of BCC to **4**. Similarly in MCH, where BCC affords a solvent insertion product in ~44−53% yield, the curved Arrhenius correlation (Figure 1) cannot be readily interpreted. In polar solvents such as TCE, clean H-shift reactions of BCC are obtained even at −71 °C; an Arrhenius correlation of LFP kinetic data is linear from 3 to −71 °C (Figure 2), affording $E_a = 3.2$ kcal mol^{-1} and log $A = 10.0$ s^{-1}. Therefore, QMT does not appear to play a major role in the 1,2-H shift rearrangement of BCC at ambient or near ambient temperature in solution.

Introduction

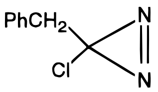
Curvature in Arrhenius correlations usually signals the active competition of 2 or more reaction channels characterized by differing activation energies. Perhaps the most interesting case is the incursion of quantum mechanical tunneling (QMT) in a classically activated process, where "the Arrhenius plot of log k against $1/T$ is nonlinear, with the curvature tending toward zero activation energy at low temperature".[5]

Such a phenomenon appears to occur in the 1,2-H shift of methylchlorocarbene (MeCCl) to vinyl chloride,[6] which suffers increasing intervention of QMT as the temperature decreases.[6a] Indeed, even at 25 °C, tunneling is believed to account for >85% of the total rearrangement.[6a] QMT is also suggested to account for two other unusual findings in this reaction: the very negative entropy of activation (−16.1 eu), and an increasing k_H/k_D for H(D) shift with *increasing* reaction temperature (from 0.9 to 1.8 as T rises from 248 to 343 K).[6a] Negative entropies of activation may simply reflect geometric constraints and are rather common for intramolecular carbenic rearrangements,[7] but the inverse temperature dependence of the kinetic isotope effect (KIE) is unusual.[8] Computational studies support the importance of tunneling in the 1,2-H shift of MeCCl, helping to rationalize both the negative $\Delta S^{\ddagger}$ and the unusual KIE temperature dependence.[9]

Benzylchlorocarbene (BCC, **1**), which is conceptually derived from MeCCl by the replacement of a hydrogen atom by a phenyl group, can be readily generated from benzylchlorodiazirine (**2**) and has been intensively studied since 1984.[7,10,11] The results have raised questions about the existence of carbene/alkene complexes,[7,10−12] the occurrence of excited diazirine rearrangements,[6b,13] and



1 (BCC)



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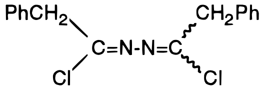

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[6] (a) Dix, E. J.; Herman, M. S.; Goodman, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 10424. (b) La Villa, J. A.; Goodman, J. L. *Tetrahedron Lett.* **1990**, *31*, 5109. (c) La Villa, J. A.; Goodman, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 6877.

[7] Moss, R. A. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press: Greenwich, CT, 1994; Vol. 1, pp 59f.

[8] Increasing KIE with increasing temperature requires a classical reaction that has an appreciable KIE over the temperature range investigated but that has a KIE that is *reduced* by the tunneling correction.[6a] Normally, QMT is associated with very large KIEs.[5]

[9] Storer, J. W.; Houk, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 10426. However, the computational results indicate that, above 200 K, the classical rate exceeds that due to tunneling, and the KIE *decreases* with increasing temperature.

[10] Tomioka, H.; Hayashi, N.; Izawa, Y.; Liu, M. T. H. *J. Am. Chem. Soc.* **1984**, *106*, 454. Liu, M. T. H.; Chishti, N. H.; Tencer, M.; Tomioka, H.; Izawa, Y. *Tetrahedron* **1984**, *40*, 887.

[11] Liu, M. T. H. *Acc. Chem. Res.* **1994**, *27*, 287.

[12] (a) Liu, M. T. H. *Chem. Commun.* **1985**, 982. (b) Bonneau, R.; Liu, M. T. H.; Kim, K. C.; Goodman, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 3829.

Table 1. Product Distributions for the Photolysis of 2 in Isooctane[a]

T (°C)	Z-**4**	E-**4**	**5**	**6**	**8**	**9**	**3**	**10**	unknown
22	14.7	74.8	6.48		1.15		1.64	1.19	
	(0.3)	(1.7)	(0.12)		(0.02)		(0.03)	(0.02)	
0	12.0	66.6	13.0		2.19		5.15	1.04	
	(0.04)	(0.2)	(0.05)		(0.01)		(0.02)	(0.00)	
−35	11.6	56.0	4.87	5.91	3.59		13.7		4.40
	(0.03)	(0.2)	(0.01)	(0.02)	(0.01)		(0.04)		(0.01)
−70	10.5	36.1	2.40	1.91	5.47	3.79	30.3		b
	(0.1)	(0.3)	(0.02)	(0.02)	(0.05)	(0.04)	(0.3)		

[a] Product distributions are taken from the averages of three capillary GC determinations as measured against a decane internal standard; errors are in parentheses. Values are not calibrated for detector response. [b] Two unknowns, 7.3 and 2.2%.

the intervention of QMT.[6a,9,14,15] For BCC, as with MeCCl, tunneling is a possibility because of curved Arrhenius correlations that attend the kinetics of the 1,2-H(D) shifts of BCC and its α,α-d_2 analogue and because of the abnormal KIE's that accompany these rearrangements.[15]

At 10−30 K in argon matrices, directly observed BCC decays by rearrangement much more rapidly than anticipated, based on extrapolations of 25 °C kinetic data. Its α,α-d_2 analogue is considerably more stable; $k_H/k_D \approx 2000$ could be estimated at 10 K. These results clearly implicate QMT in the 1,2-H shift of BCC at a cryogenic temperature,[14] while the parallel behavior of MeCCl and BCC (curved Arrhenius correlations, abnormal KIE's) at a higher temperature[6a,15] suggests that tunneling could also be important for BCC at higher temperatures. A very careful examination of BCC chemistry is required to evaluate this possibility.

Much information has already been acquired. Thermolysis or photolysis of **2** in CCl_4 or benzene yielded Z- and E-β-chlorostyrenes, attributed to the 1,2-H shift of BCC.[10] Initial laser flash photolytic (LFP) kinetic studies from 0 to 31 °C, carried out either by direct observation of the BCC or by the pyridine ylide method,[16] gave *linear* Arrhenius correlations and activation parameters of $E_a = 4.83 \pm 0.24$ kcal mol^{-1}, log $A = 11.28 \pm 0.20$ s^{-1}, or $E_a = 4.5 \pm 0.3$ kcal mol^{-1}, log $A = 11.1 \pm 0.2$ s^{-1}, respectively.[17] At 24 °C, k(1,2-H) was 5.4×10^7 s^{-1}. Comparable data were later obtained for para-substituted BCC, where the substituents included CF_3, Cl, Me, and MeO.[18]

The unusual Arrhenius behavior of MeCCl[6] induced Liu and Bonneau to extend the temperature range[15] of their initial[17] BCC kinetic studies. The linearity observed over the 0−31 °C temperature range[17] disappeared when the decay kinetics of BCC and BCC-d_2 were studied in isooctane from −80 to 60 °C.[15] For BCC, the rate constant first decreased with decreasing temperature and then leveled off at −40 °C; with BCC-d_2, leveling occurred at −10 °C. The limiting rates of carbene decay converged at 1×10^7 s^{-1} for both carbenes[15] and as with MeCCl,[6a] the KIE for BCC/BCC-d_2 appeared to increase with increasing temperature (viz., $k_H/k_D = 0.87$ at −50 °C and 2.62 at 30 °C).[15] The Arrhenius curvature was attributed either to competitive intermolecular reactions of BCC with the isooctane solvent (although no product corresponding to this reaction was reported;[15] see below) or to the incursion of QMT.

The QMT hypothesis would be strengthened if it could be shown that products derived from intermolecular reactions are absent. For example, formation of azine **3** by an intermolecular reaction of BCC with diazirine **2**, in competition with the intramolecular 1,2-H carbene rearrangement, offers an alternative explanation for the curved Arrhenius correlation: if the E_a for azine formation were significantly lower than that for the 1,2-H shift, the Arrhenius correlation of the rate constants for carbene decay would flatten out as the temperature decreased. In the case of MeCCl, where azine is known to form, this problem was addressed by "correcting" the kinetics of carbene decay, at each temperature of measurement, by extrapolation of the associated rate constant to its value at [diazirine] = 0.[6a] What about BCC?

A reinvestigation showed that photolytically generated BCC did yield azine **3** by reaction with **2**; in *neat* diazirine, 40% of Z/E-**3**, 40% of the 1,2-H shift products, Z/E-**4**, 10% of the 1,2-Ph shift product **5**, and 10% of the carbene-HCl addition product **6** were formed.[19] The rate constant for azine formation was determined by LFP to be $(3.6 \pm 0.4) \times 10^8$ M^{-1} s^{-1}, but this reaction was considered to be important only at high [**2**]: under the LFP conditions employed in the Arrhenius studies of BCC, azine **3** was not reported, and it was not observed when 10 mM **2** was decomposed to 20% conversion at −80 °C in isooctane.[15]

$PhCH{=}CHCl$ $PhCCl{=}CH_2$ $PhCH_2CHCl_2$

(Z/E)-**4** **5** **6**

On the other hand, a recent study of the kinetics and activation parameters associated with the 1,2-rearrangements of the BCC analogue mesitylmethylchlorocarbene **7** (and **7**-α,α-d_2) revealed curved Arrhenius correlations that were definitely associated with competitive azine formation.[20] At a concentration of 20 mM diazirine precursor, Arrhenius correlations for **7** and **7**-d_2 were curved, and significant azine formation was observed at −35 and −70 °C. However, when the diazirine concentration was reduced to 10 mM, the Arrhenius correlation remained linear to −70 °C.[20] Moreover, with relevance to the present report, a preliminary reinvestigation of the **2**/BCC system revealed that up to 30% of azine **3** formed when 15 mM **2** was photolytically decomposed in isooctane at −70 °C, suggesting that competitive azine forma-

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(16) Jackson, J. E.; Soundararajan, N.; Platz, M. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1988**, *110*, 5595.

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(18) Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1992**, *114*, 3604.

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(20) Moss, R. A.; Merrer, D. C. *Chem. Commun.* **1997**, 617.

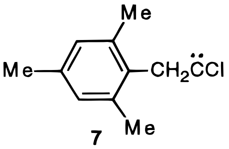
tion was at least a contributing cause of the Arrhenius curvature attending the rearrangement of BCC.[20]

Herein, we provide a full account of our joint reinvestigation of the products and the kinetics for the reactions of BCC as generated from benzylchlorodiazirine. Included are new studies of solvent and temperature dependence.

Results

Product Studies. Solutions of **2** in isooctane containing a decane internal standard (0.014 M, $A_{344} = 0.7$) were photolyzed in a Rayonet reactor (350 nm) until all the diazirine was destroyed (UV). The photolyses were conducted at 22, 0, −35, or −70 °C, and the product solutions were analyzed by capillary GC and GC−MS. Table 1 summarizes the product distributions.

In addition to the H-shift products, *β*-chlorostyrenes *Z*-**4** and *E*-**4**, the Ph-shift α-chlorostyrene **5**, and the HCl addition product **6**, we also observed a BCC−isooctane insertion product **8**, BCC dimer(s) **9**, the azine **3**, and (traces of) benzyl chloride **10**. Products **4**−**6** were identified by comparisons of GC retention times and NMR spectra to those of authentic or previously reported samples.[19,21] Products **8**, **9**, and **10** were assigned by GC−MS; the structure of **8** is uncertain, although it probably corresponds to BCC insertion into the tertiary C−H bond of isooctane. Azine **3** was prepared by a "preparative" photolysis of **2** in isooctane ($A_{344} \approx 1.0$) with purification by silica gel chromatography. The assignment of the structure rests on NMR, MS, and an exact mass determination.



7

$PhCH_2CHCl\text{-}C_8H_{17}$

8

$PhCH_2CCl{=}ClCCH_2Ph$

(*Z*/*E*)-**9**

$PhCH_2Cl$

10

Table 1 reveals that the product mixture derived from BCC becomes more complex with decreasing reaction temperature. Notable are the now documented appearances of the isooctane insertion product **8**, carbene dimer **9**, and azine **3**. Their contributions are greatest in the −70 °C photolysis, where azine constitutes 30% of the product. These trends parallel our observations with carbene **7**.[20]

Reactions in Methylcyclohexane. Photolyses of diazirine **2** were also carried out in methylcyclohexane (MCH) for comparison to the studies in isooctane. BCC and BCC-α,α-d_2 were photolytically generated from the diazirines at [**2**] = 18 or 8.5 mM. Carbene decay was monitored directly at 310 nm as a function of temperature (20 to −78 °C) in LFP experiments; the results are shown as Arrhenius correlations in Figure 1.

Curvature is very apparent in the 18 mM BCC-d_2 correlation, whereas it appears to be more gentle in the 8.5 mM BCC correlation, with an onset at lower temperature.[22] It was impractical to use lower diazirine concentrations because of insufficiently intense carbene signals during the LFP experiments.

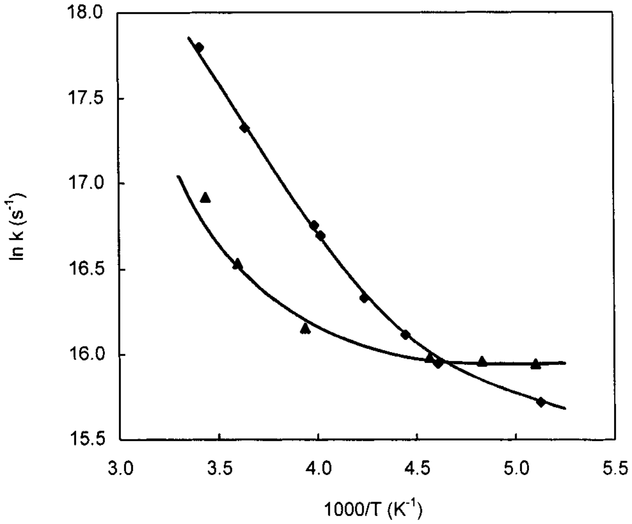


Figure 1. Arrhenius correlations for BCC in MCH: (◆) 8.5 mM **2**, (▲) 18 mM **2**-d_2.

At first glance, the results appear consistent with the isooctane findings, where azine formation is a principal cause of Arrhenius curvature. Azine **3** also forms in these MCH experiments as evidenced by UV examination of spent photolysis mixtures, in which the broad azine absorption can be seen between 300 and 330 nm and is enhanced at −80 °C, relative to the 22 °C photolyzates.

However, product studies by GC−MS reveal that the BCC−MCH photolyses are complicated in a way different from that of the isooctane studies: in MCH, azine is a minor contaminant, but BCC insertion into the MCH becomes a major problem. At 25 °C, with [**2**] = 18 mM, GC−MS examination of the photolyzate reveals 15.3% of *Z*-**4**, 69.0% of *E*-**4**, 1.2% of azine **3**, and 14.4% of a BCC−MCH product (*m*/*e* 236, 238). At −75 °C, with [**2**] = 18 mM, BCC−MCH increases to 44%, while *Z*/*E*-**4** drops to only 23% of the product mixture. Azine **3** (4.5%) is a minor constituent, but two unknowns comprise 29% of the product mixture. The results are no better at [**2**] = 8.5 mM at −75 °C, when BCC−MCH constitutes 53% of the products, but alkenes **4** are only 24%. Azine is reduced to 2.6%, but unknowns contribute 21%.

Clearly, the low-temperature LFP data of Figure 1 do not mainly reflect carbenic decay via the 1,2-H shift, and they are not very useful for further analysis. The facile low-temperature reaction of BCC with MCH, however, is of considerable interest and will be further examined.

Studies in Tetrachloroethane. Earlier experiments demonstrated that the 1,2-H rearrangements of BCC (or BCC-d_2) exhibited *linear* Arrhenius behavior in solvent $CHCl_3$ from 60 to −55 °C; for BCC the Arrhenius parameters were $E_a = 3.6$ kcal mol^{-1} and log $A = 10.4$.[15] The change from curved to linear Arrhenius correlation as the solvent is altered from isooctane to chloroform has been associated with a more efficient 1,2-H shift (relative to intermolecular reactions in the more polar solvent).[23] Such an effect is very marked with benzylfluorocarbene ($PhCH_2CF$, BFC) photolytically generated from ben-

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(21) Liu, M. T. H.; Subramanian, R. *J. Org. Chem.* **1985**, *50*, 3218.

(22) The results at least superficially resemble those obtained[15] with BCC and BCC-d_2 using 10 mM [**2**] in isooctane.

(23) Polar solvents stabilize the "polar" 1,2-H shift transition state: see ref 13b, and Sugiyama, M. J.; Celebi, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 966. The more negative $\Delta S^{\ddagger}$ observed in the polar solvents may reflect enhanced solvation of the H-shift transition state.

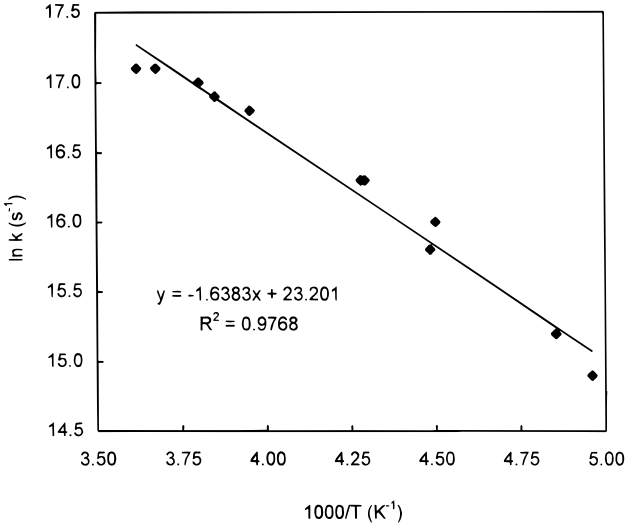

Figure 2. Arrhenius correlation for BCC in TCE ([**2**] = 22 mM).

zylfluorodiazirine. In hydrocarbon solvents at 25 °C, this carbene's H-shift products are accompanied by 20−38% of azine, whereas in the polar solvent 1,1,2,2-tetrachloroethane (TCE), azine formation is reduced to 6%.[24]

The kinetics of BFC rearrangement have been determined in TCE,[24] so for purposes of comparison, the BCC rearrangement was examined in this solvent. The product distribution, in contrast to that of the isooctane or MCH cases, is uncomplicated. Samples of diazirine **2** (~22 mM) were completely photolyzed in the Rayonet reactor ($\lambda = 350$ nm) at 22, 0, −35, or −70 °C. Products were analyzed by capillary GC against an internal decane standard. Only *Z*- and *E*-**4** were found at each temperature, with *Z*/*E* distributions ranging from 18:82 (−70 °C) to 22:78 (22 °C). Even at −70 °C, no azine or other additional products could be found.

LFP kinetic studies of the BCC → **4** H-shift in TCE utilized the pyridine ylide method,[16] which afforded a stronger signal than direct observation of BCC. After the 351-nm laser flash, growth of the BCC−pyridine ylide signal was followed at 370 nm in TCE solutions containing 22 mM **2** and 1.4−9.0 mM pyridine. Extrapolation of the linear correlation of k_{obs} for ylide formation vs [pyridine] to [pyridine] = 0 then afforded a *Y* intercept which, in view of the very clean BCC → **4** rearrangement, could be taken as k_{re} for the 1,2-H shift in TCE. At 0 °C, for instance, k_{re} was 2.67×10^7 s^{-1}. Repetition of these determinations at 11 temperatures from 3.2 to −71.4 °C afforded 11 rate constants which appear as an Arrhenius correlation in Figure 2. In contrast to the curvature observed in isooctane[15] or MCH (see Figure 1), good linearity ($r = 0.988$) is obtained in TCE (as in $CHCl_3$[15]). The Arrhenius parameters in TCE are $E_a = 3.2$ kcal mol^{-1} and $\log A = 10.0$ s^{-1}, corresponding to $\Delta S^{\ddagger} = -14.5$ eu (at 25 °C), which compare quite well with the earlier determinations in $CHCl_3$.[15]

In both TCE ($\epsilon = 8.20$)[25] and $CHCl_3$ ($\epsilon = 4.81$),[25] the intramolecular hydride shift is potentiated, effectively shutting off alternative intermolecular chemistry (e.g., azine formation, solvent insertion). Linear Arrhenius behavior occurs for BCC, together with simplification of its chemistry. Parallel experiments indicate that analogous results can be obtained in other, nonhalogenated polar solvents, such as methyl benzoate ($\epsilon = 6.59$)[25] or ethyl acetate ($\epsilon = 6.11$).[25]

Discussion

Curved Arrhenius correlations for 1,2-H shift carbenic rearrangements have been reported for MeCCl,[6] $MesCH_2$-CCl (**7**),[20] and BCC (**1**).[15] For temperatures down to at least −70 °C, it is clear that the curvature for **7** is mostly due to competition between (intramolecular) 1,2-H rearrangement and (intermolecular) azine formation.[20] The latter process is effectively temperature independent and must have a near zero activation energy,[26] so that it becomes increasingly important at low temperature.

For BCC, the product studies of Table 1 clearly reveal the presence of azine **3**, solvent insertion product **8**, and carbene dimer **9** in a total yield of ~40% at −70 °C and in lesser but still significant quantities at higher temperatures. Again, curvature in the Arrhenius correlations obtained in isooctane[15] or in MCH (Figure 1) can be attributed to competitive intermolecular reactions, with solvent insertion of particular significance in MCH.

A reviewer has suggested that we "correct" the BCC Arrhenius correlation for the incursion of azine **3** using the measured rate constant for the reaction of BCC and diazirine **2**.[26] When this is done, the curvature is "straightened" and its onset is moved to lower temperature (i.e., from −45 °C before correction to −60 °C after correction). This is in keeping with our suggestion that, as with carbene **7**,[20] much or all of the Arrhenius curvature exhibited by BCC above −70 °C is associated with competing intermolecular reactions. Nevertheless, the reviewer notes that bimolecular reactions (such as azine formation) and tunneling could have similar activation parameters and might occur together, making their differentiation very difficult.

We suggest that QMT plays a relatively minor role in the BCC 1,2-H shift at temperatures above −70 °C in solution. At lower temperatures, we may expect an incursion of QMT. This would not be surprising because QMT is known to govern the 1,2-H shift of BCC in argon matrices at 30 K.[14] What is yet unknown is the contribution of QMT to the BCC H-shift between −243 and −70 °C. At what temperature does its contribution equal or exceed that of the classical rearrangement? Is QMT important beyond cryogenic conditions? It will be difficult to answer these questions experimentally because of the competitive intermolecular reactions encountered at low temperatures, but LFP studies in high-melting matrices or in viscous nonpolar fluids may provide new information.

For BCC, two remaining observations, a significantly negative $\Delta S^{\ddagger}$ for the 1,2-H shift and a KIE that increases with increasing temperature, require comment. A negative activation entropy is common in 1,2-H (and 1,2-C) carbenic rearrangements[7] and can be associated with the unusual geometries of these rearrangements that engen-

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(24) Moss, R. A.; Maksimovic, L.; Merrer, D. C. *Tetrahedron Lett.* **1997**, *38*, 7049.

(25) Dean, J. A., Ed. *Lange's Handbook of Chemistry*, 14th ed.; McGraw-Hill: New York, 1992; p 5.91−5.125.

(26) For example, k_q for azine formation from BCC and **2** is $(3.6 \pm 0.4) \times 10^8$ M^{-1} s^{-1} in isooctane at 25 °C[19] and $(3.15 \pm 0.3) \times 10^8$ M^{-1} s^{-1} in MCH at −90 °C (this work). The rate constants were obtained by LFP, following the rate of decay of BCC as a function of [**2**].

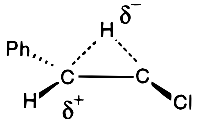
(27) Moss, R. A.; Ho, G.-J.; Shen. S.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1990**, *112*, 1638. Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 470.

der reduced transmission coefficients across the activation barriers.[27] The unusual temperature dependence of the KIE may be suspect at lower temperatures because the k_H and k_D values were obtained by interpolations on smooth curves drawn through experimental rate constants that are now known to have been "contaminated" by intermolecular reactions. However, increasing KIEs (2.00−2.62) from 0 to 30 °C remain unexplained and are analogous to the KIEs observed with MeCCl, where the unusual temperature dependence has been ascribed to QMT.[6a,9]

Presently, MeCCl is the only known carbene for which tunneling at ambient temperatures is considered to make a major contribution to the 1,2-H shift.[6a,9] A priori, one would expect that the phenyl "substitution" that converts MeCCl to BCC should lower the E_a for the classical 1,2-H shift of BCC, relative to MeCCl, and also lower the temperature at which QMT would come to dominate the classical H-shift mechanism. Ab initio computations[28,29] clearly display the anticipated ΔE_a, but experimental results for MeCCl[6a] and BCC (see Table 2) indicate a smaller ΔE_a between these carbenes.

The activation energy for the 1,2-H shift of BCC has now been determined several times in isooctane, $CHCl_3$, and TCE; the data are collected in Table 2, entries 1−4. Given the influence of competing intermolecular reactions in isooctane and the uncertainties attending correction of the data (entry 2), it is difficult to obtain a precise set of activation parameters. The value obtained in isooctane at 0−31 °C, where intermolecular reactions are minimal, is $E_a = 4.8$ kcal mol^{-1}.[17] It is the best hydrocarbon solvent value currently available, though it does not differ experimentally from the value for MeCCl ($E_a = 4.9 \pm 0.5$ kcal mol^{-1}).[6c] Under these conditions, the activation entropy for the BCC 1,2-H shift is moderately negative at ∼−9 eu ($\Delta S^{\ddagger} \sim -16$ eu for MeCCl).[6c]

In polar solvents such as $CHCl_3$ or TCE (entries 3 or 4, Table 2), the activation energy for 1,2-H migration is reduced by ∼1−1.5 kcal mol^{-1}, presumably due to stabilization of the polar transition state **11** by the polar solvent.[23] These small decreases in the E_a for BCC rearrangement appear to be dramatically reflected in the product composition, which is remarkably clean in the polar solvents. In contrast to the complexity caused by the incursion of intermolecular reactions in isooctane or MCH, in $CHCl_3$[15] or TCE, only the intramolecular BCC H-shift products *Z*- and *E*-**4** are observed.



11

A similar sensitivity to solvent was observed with benzylfluorocarbene (BFC), where 25 °C photolysis of the corresponding diazirine (11.6 mM) in various hydrocarbon solvents gave 20−38% of the azine in addition to 62−80% of the expected β-fluorostyrene H-shift products.[24]

Table 2. Arrhenius Parameters for Rearrangement of BCC and BFC[a]

entry	carbene	conditions	E_a, kcal mol^{-1}	log *A*, s^{-1}	$\Delta S^{\ddagger}$, eu	ref
1	BCC	isooctane, 31 to 0 °C[b]	4.8	11.3	−8.9	*c*
2	BCC	isooctane, 60 to −42 °C[d]	5.8	11.9	−6.2	*e*
3	BCC	$CHCl_3$, 60 to −55 °C	3.6	10.4	−12.9	*e*
4	BCC	TCE, 3 to −71 °C	3.2	10.0	−14.5	*f*
5	BFC	TCE, 66 to −68 °C	3.2	9.5	−17.2	*g*

[a] At 298 K. Estimated errors are ±0.5 kcal mol^{-1} in E_a. [b] Data are for the direct observation of BCC. [c] Reference 17. [d] Corrected for reaction with the solvent, assuming $k = 9 \times 10^6$ s^{-1} for this reaction. The main intermolecular reaction, however, is azine formation, see above. [e] Reference 15. [f] This work. [g] Reference 24; the activation parameters are means of three determinations, with errors of ±10% in E_a and ±2.4% in log *A*.

In TCE, however, the azine yield was reduced to 6%, while variable temperature LFP studies afforded the activation parameters shown in Table 2 (entry 5).

Surprisingly, the activation parameters for the 1,2-H shifts of BCC and BFC in TCE differ by only 2.7 eu in $\Delta S^{\ddagger}$, favoring ∼4−5-fold faster rearrangement of the chlorocarbene.[24] This modest difference suffices to produce ∼50% of azine from BFC at −50 °C, even in TCE,[24] whereas no azine is detected in comparable BCC reactions. The cautionary message is that major contamination of intramolecular carbenic rearrangements by intermolecular side reactions can be induced by very small changes in the activation parameters. Careful attention to experimental factors such as precursor concentration, solvent, and reaction temperature are essential to obtaining uncomplicated product mixtures and interpretable kinetic data.

Conclusions

The Arrhenius curvature observed for the rate constants of the 1,2-H rearrangement of BCC in hydrocarbon solvents is mainly due to competitive intermolecular chemistry (azine formation, solvent insertion) down to a temperature of −60 to −70 °C. In this regard, the chemistry of BCC resembles that of its mesityl analogue **7**.[20] In polar solvents ($CHCl_3$, TCE), the products formed from BCC are solely the intramolecular H-shift isomeric β-chlorostyrenes **4**; no intermolecular products are encountered, even at −70 °C. Rate constants and activation parameters were determined for the BCC 1,2-H shift in several solvents: the activation energies are ∼3.2 kcal mol^{-1} in the polar solvents and ∼4.8 kcal mol^{-1} in the hydrocarbon solvent; the entropy of activation is negative, ranging from ∼−6 to −14 eu, depending on the solvent, conditions of measurement, and corrections applied to the data. QMT does not appear to play a major role in the 1,2-H shift rearrangement of BCC at ambient or near ambient temperatures in solution. At temperatures below −70 °C, however, QMT may contribute significantly; by −243 °C, its influence is dominant.[14]

Experimental Section

General. Proton NMR spectra were determined on a Varian VXR-200 spectrometer (200 MHz). Chemical shifts are reported as ppm (δ) relative to TMS. GC−MS data were obtained on a Hewlett-Packard (HP) 5890 GC (column: HP5) equipped with an HP 5971 mass selective detector. High-resolution mass spectra (HRMS) were recorded on a VG ZAB-T double-focusing mass spectrometer. Capillary GC analyses

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(28) Calculated (B3LYP/6-31G*, with ZPE corrections) values of E_a for 1,2-H shifts of MeCCl and BCC are 12.9 and 6.8 kcal mol^{-1}, respectively,[29] although these values are clearly too high; e.g., the experimental value of E_a for the 1,2-H shift of MeCCl is ∼5 kcal mol^{-1}.[6c] Small curvature tunneling corrections reduce the classical, calculated E_a for MeCCl to 8.8 kcal mol^{-1}.

(29) Keating, A. E.; Houk, K. N. Private communication, August 4, 1997.

were acquired on a Varian 3700 GC with a flame ionization detector (injector 200 °C, detector 290 °C) connected to a Varian 4270 integrator. For all analytical GC data, we used a 25 m × 0.25 mm × 0.25 μm Chrompack CP-Sil 5CB (Chrompack, Inc., Raritan, NJ), chemically bonded 100% dimethyl polysiloxane column. Radial preparative TLC was conducted on a Chromatotron with a silica gel rotor (2 mm thickness, Analtech, Inc., Newark, DE). Photolyses were performed in a Rayonet photochemical reactor equipped with 16 RPR-3500 bulbs (λ = 350 nm). Constant-temperature photolyses utilized a Pyrex Dewar flask and a methanol−dry ice bath. UV spectra were obtained on an HP 8451 diode array spectrophotometer.

All chemicals were purchased from Aldrich Chemical Co. unless otherwise noted. Hydrogen chloride and ammonia gases were purchased from Matheson Gas Products, E. Rutherford, NJ. Pyridine was dried by distillation from CaH_2 and stored over molecular sieves. *sym*-Tetrachloroethane was dried over $CaCl_2$. All other chemicals were used as received. A 10% decane solution in isooctane was used as an internal standard in all thermolyses and photolyses unless otherwise noted.

LFP experiments in TCE utilized a Lambda Physik EMG 101 XeF excimer laser. The laser produced pulses at 351 nm with a 14-ns duration at an average power of 35−50 mJ/pulse.[30] Data were processed with Igor Pro 2.0 software (Wavemetrics, Inc.) on a Macintosh IIsi personal computer. Suprasil quartz cuvettes (1 × 1 cm) were used to hold the samples. For variable-temperature experiments, the sample cell was equilibrated in an ethanol or an ethanol−dry ice bath of the appropriate temperature before insertion in the sample holder. The temperature of the sample at the instant of the laser flash was measured by an indwelling thermocouple connected to a digital thermometer. LFP experiments in MCH utilized 355-nm light (third harmonic) from a Nd:YAG laser. This system has also been described previously.[31]

3-Chloro-3-benzyldiazirine (2). The diazirine was prepared by hypochlorite oxidation[32] of benzylamidinium hydrochloride,[33] mp 145−148 °C. A mixture of 7.0 g of LiCl and 3.0 g (0.018 mol) of benzylamidinium hydrochloride in 100 mL of DMSO and 100 mL of pentane was placed in a 1-L, three-necked round-bottom flask fitted with a dropping funnel, mechanical stirrer, and a thermometer. Aqueous NaOCl solution (150−200 mL; "pool chlorine", 11% OCl^-) saturated with NaCl was added with stirring to the mixture; the temperature was maintained at 35−40 °C. During the reaction, an additional 50 mL of pentane was added. After addition of the NaOCl solution was completed, the mixture was stirred at room temperature for 30 min. The pentane layer was washed with 3 × 1000 mL of water and dried over $CaCl_2$. The diazirine solution was purified by chromatography on silica gel (pentane eluent) to afford diazirine **2**, λ_{max} = 344, 346, 356 nm.

Thermolysis of Diazirine 2 in Isooctane. A solution of **2** in isooctane (A_{344} = 0.65) was placed in a screw-top Pyrex pressure tube and heated in the dark in an oil bath at 105 °C for 5.5 h. Capillary GC analysis revealed the hydride-shift products *Z*- and *E*-**4** (> 98% total yield); the *Z*/*E* ratio was 1:7.

The identity of *Z*-**4** was confirmed by comparison of its NMR spectrum with the reported spectrum[21] and by GC−MS. ^{1}H NMR ($CDCl_3$): 6.28 and 6.65 (AB q, J_{AB} = 8.4 Hz, 2H); 7.31 (s, 5H). GC−MS: *m*/*e* (rel intensity) 138, 140 (80:24, M^+, $M^+ + 2$), 103 (base peak, $M^+ - 35$).

The structure of *E*-**4** was confirmed by comparison of its NMR spectrum with the previous report[21] and by GC−MS. ^{1}H NMR ($CDCl_3$): 6.64 and 6.85 (AB q, J_{AB} = 13.7 Hz, 2H); 7.31 (s, 5H). GC−MS: *m*/*e* (rel intensity) 138, 140 (65:22, M^+, $M^+ + 2$), 103 (base peak, $M^+ - 35$).

Photolyses of Diazirine 2 in Isooctane. Solutions of **2** in isooctane (A_{344} = 0.7, 2.0 mL) were contained in sealed quartz cuvettes and photolyzed at 22, 0, −35, or −70 °C until all the diazirine had been destroyed in each sample (20−40 min). The products were analyzed by capillary GC and GC−MS. Products **5** and **6** were identified by NMR and GC comparisons with authentic samples (see below). Product **8** (insertion of BCC into a C−H bond of isooctane) and product **9** (dimer of BCC) were identified by GC−MS. Azine **3** was prepared as described below and purified by chromatography on silica gel.

α-Chlorostyrene (5). A 100-mL, three-necked round-bottom flask was fitted with a rubber septum, a condenser topped with an N_2 inlet, and a thermometer. Into the N_2-purged system was placed 11.0 g (0.053 mol) of PCl_5. To this was slowly added with stirring 9.0 mL (0.075 mol) of acetophenone. The reaction mixture was heated at 80 °C for 70 min. ^{1}H NMR and GC−MS of the crude product revealed >90% of **5**. The NMR spectrum ($CDCl_3$) compared well with the previously reported data:[34] 5.52 and 5.77 (AB q, J_{AB} = 1.6 Hz, 2H); 7.35 (m, 5H). GC−MS: *m*/*e* (rel intensity) 138, 140 (46:16, M^+, $M^+ + 2$), 103 (base peak, $M^+ - 35$).

1,1-Dichloro-2-phenylethane (6). A solution of benzylchlorodiazirine (**2**) in 1.0 M HCl/ether ($A_{342} \approx 2.0$, 10 mL) was placed in a screw-top Pyrex pressure tube and photolyzed for 3 h at room temperature in the Rayonet reactor. The reaction was complete when the yellow reaction solution turned colorless. Excess HCl was removed by vacuum with a water aspirator, and dichloride **6** was isolated by radial preparative TLC on silica gel (pentane eluent). Fraction 1 contained β-chlorostyrenes (**4**); fraction 2 contained the desired product. ^{1}H NMR data matched the data previously reported by Liu.[21] ^{1}H NMR ($CDCl_3$): 3.46 (d, *J* = 6.42 Hz, 2H); 5.83 (t, *J* = 6.43 Hz, 1H); 7.31 (s, 5H). GC−MS: *m*/*e* (rel intensity) 174, 176, 178 (9.3:5.3:1.3, M^+, $M^+ + 2$, $M^+ + 4$), 159, 161, 163 (47:29:5.3, $M^+ - 15$), 91 (base peak, $M^+ - 83$).

Products 8 and 9. Chromatographic fractions from the isolation of azine **3**, which contained isooctane insertion product **8** and dimer **9** were analyzed by GC−MS: **8** *m*/*e* (rel intensity) 252 (1.3, M^+), 145 (6.9, $M^+ - 107$), 131 (5.0, $M^+ - 121$), 113 (20, $M^+ - 139$), 91 (36.3, $M^+ - 161$), 57 (base peak, $M^+ - 195$). **9** *m*/*e* (rel intensity) 276, 278, 280 (44.7:29.8:5.1, M^+, $M^+ + 2$, $M^+ + 4$), 205 (44.7, $M^+ - 71$), 163 (88.1, $M^+ - 113$), 91 (base peak, $M^+ - 185$).

Azine 3.[19] Several 4.0-mL samples of **2** in isooctane ($A_{344} \approx 1.0$) were photolyzed at −70 °C for 20 min each. After photolysis, the product mixtures were combined, and crude **3** was purified by column chromatography on silica gel (pentane eluent). ^{1}H NMR ($CDCl_3$): 3.97 (s, 4H); 7.34 (s, 10H). GC−MS: *m*/*e* (rel intensity) 304, 306, 308 (10.6:7.5:2.5, M^+, $M^+ + 2$, $M^+ + 4$)], 269 (13.8, $M^+ - 35$), 116 (base peak, $M^+ - 188$), 91 (90, $M^+ - 213$). HRMS (EI): exact mass for $C_{16}H_{14}N_2Cl_2$ calcd, *m*/*e* 304.053 404; observed, 304.053 367.

Photolyses of Diazirine 2 in Methylcyclohexane. These experiments were conducted at [**2**] = 18 or 8.5 mM in MCH at 25 or −75 °C in a manner analogous to that of the isooctane photolyses (see above). The product distributions are discussed in the Results section. The BCC−MCH product was identified by GC−MS: *m*/*e* (rel intensity) 236, 238 (13:4.3, M^+, $M^+ + 2$); 128 (10, $M^+ - 108$); 97 (base peak, $M^+ - 139$); 91 (55, $M^+ - 145$); 55 (41, $M^+ - 181$).

LFP Studies in Tetrachloroethane. Solutions of **2** in *sym*-tetrachloroethane (A_{346} = 1.0) containing (1.4−9.0) × 10^{-3} M of pyridine (2.0 mL total) were irradiated with an XeF excimer laser (λ = 351 nm) at selected temperatures over a range of −71 to +3 °C. The formation of the BCC−pyridine ylide was monitored at 370 nm.

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[30] For a description of this installation, see Moss, R. A.; Shen, S.; Hadel, L. M.; Kmiecik-Lawrynowicz, G.; Wlostowska, J.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1987**, *109*, 4341 and Moss, R. A.; Xue, S.; Liu, W.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1996**, *118*, 12588.

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For product studies, samples of **2** in TCE (A_{346} = 1.0, 2.0 mL) were placed in sealed quartz cuvettes and irradiated in the Rayonet reactor at −70, −35, 0, and 22 °C for 40 min. Capillary GC analysis revealed only β-chlorostyrenes *Z*- and *E*-**4** as the products in all cases.

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