Absolute kinetics of mesitylmethylchlorocarbene reactions

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Absolute rate constants were determined for reactions of mesitylmethylchlorocarbene, which affords intramolecular products derived from 1,2-H migration, 1,2-mesityl migration, and C–H insertion; at −35 or −70 °C, however, the intrusion of intermolecular channels affords azine and carbene dimer, complicating interpretations of the kinetics.

Over the past dozen years, the chemistry of benzylchlorocarbene, **1**, has provided a rich complement of contemporary puzzles in carbene chemistry.[1] Continuing kinetics studies have raised questions about the relevance of carbene/alkene complexes,[2] excited carbene precursors[3] and quantum mechanical tunnelling[4] during the 1,2-H migration of **1**, as well as the origin(s) of curved Arrhenius correlations[4b,c,5] and abnormal kinetic isotope effects[4] in these same rearrangements.

Our own interest in these matters[1b,d] impelled us to open a new investigation from the perspective of the related mesitylmethylchlorocarbene, **2**. Although our results partly accord with findings in the benzyl system, they raise important questions concerning the influence of competitive intermolecular carbene reactions at moderately low temperatures.

Carbene **2** and [α,α-$^2H_2$]-**2** were generated by photolysis or thermolysis of the corresponding diazirine precursors,[6] **3** and [α,α-$^2H_2$]-**3**: λ_{max} (pentane) 342, 348 (346 for [$^2H_2$]-**3**), 358 nm; ε_{342} = 50 dm^3 mol^{-1} cm^{-1} ($CDCl_3$). For the generation of **2**, we initially employed diazirine solutions with A_{342} *ca.* 1.0–1.1; [**3**] *ca.* 0.02 mol dm^{-3}. Photolysis of **3** (isooctane, 25 °C, λ > 300 nm) was continued until the diazirine was destroyed, and afforded products **4**–**7**, attributed to carbene **2** in > 96% yield.

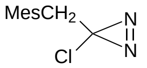
The product distributions from carbenes **2** and [$^2H_2$]-**2** were determined relative to an internal decane standard (±2%) and appear below. We obtained 1,2-H-rearranged alkenes *Z*- and *E*-(2-chloroethenyl)mesitylene (**4** and **5**), 1,2-mesityl shifted (1-chloroethenyl)mesitylene (**6**) and methyl insertion product 2-chloro-1,3-dihydro-4,6-dimethylindane (**7**). Thermolysis [pentane, sealed tube, 80 °C (**3**) or 100 °C ([$^2H_2$]-**3**), 36 h] led to distributions that were quite similar to those from photolysis. Comparison of the yields of (**4** + **5**) *vs.* (**6** + **7**) from **2** and its [α,α-$^2H_2$] analogue point to a substantial primary kinetic isotope effect (KIE) associated with the H(D) shift. This is discussed below.

$PhCH_2\ddot{C}Cl$

1

$MesCH_2\ddot{C}Cl$

2



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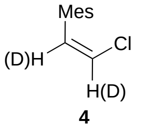

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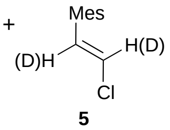

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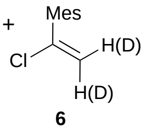

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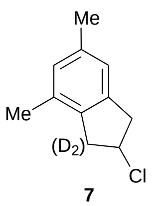

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	4	**5**	**6**	**7**
2:	58	19	5	18 (%)
[$^2H_2$]-**2**:	36	14	11	39 (%)

Photolyses of **3** in the presence of 2-methylbut-1-ene led to **4**–**7** and the carbene/alkene addition products, *Z*- and *E*-1-chloro-1-mesitylmethyl-2-ethyl-2-methylcyclopropanes. When photolyses of **3** or [$^2H_2$]-**3** were performed in the presence of increasing concentrations of the alkene in isooctane, correlations of (addition/intramolecular products) *vs.* [alkene] were curved for each of the intramolecular products. However, the inverse correlations of (intramolecular/addition products) *vs.* 1/[alkene] were each linear.

If we assume that the second product-forming intermediate (in addition to carbene **2**) demanded by these results is excited diazirine **3***,[3] rather than a carbene/alkene complex,[2] then the *y*-intercepts of the inverse correlations give the partitions of **3*** between N_2-loss to **2** or direct formation of **4**–**7**.[1b,c,3] Product formation from **3*** is then (**4** + **5**) 17.5; **6**, 1.4; and **7**, 4.7%. From [$^2H_2$]-**3***, the corresponding values are 24.5, 3.4 and 10.6%, respectively. The balance of each product comes from the carbene, and the 'raw' product yields can be 'corrected' and renormalized to afford carbene-only distributions:[7] (from **2**) (**4** + **5**), 74.3; **6**, 5.7; **7**, 20.0%; (from [$^2H_2$]-**2**) (**4** + **5**), 45.4; **6**, 12.7; **7**, 41.9%. These data are used below to partition the global rate constants for carbene decay.

Global rate constants for the disappearance of carbenes **2** or [$^2H_2$]-**2** were obtained by laser flash photolysis (LFP) at 351 nm of the diazirines in isooctane. Carbene decay was followed directly at 310–313 nm and from −70 to 47 °C. Rate constants are considered accurate to ±10%.

Fig. 1 illustrates the Arrhenius correlations of ln *k* *vs.* T^{-1} for the carbene decays. Linearity is observed for **2** down to *ca.* −40 °C, and for [$^2H_2$]-**2** to *ca.* −20 °C, after which the observed rate constants begin to level off with convergence at *k* *ca.* 9 × 10^5 s^{-1} (ln *k* *ca.* 13.7). This behaviour resembles that of **1** and

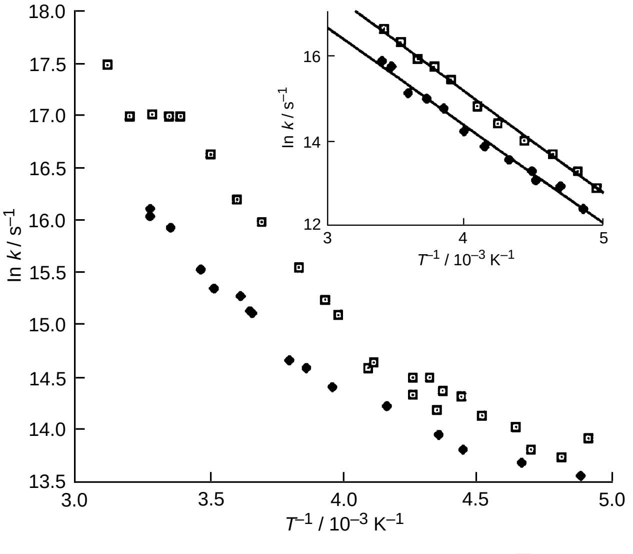

Fig. 1 Arrhenius correlations for the decays of carbenes **2** (⊡) and [α,α-$^2H_2$]-**2** (◆); A_{342} *ca.* 1.0. Inset: Arrhenius correlations for the decays of carbenes **2** (⊡) and [α,α-$^2H_2$]-**2** (◆); A_{342} *ca.* 0.5.

[$^2H_2$]-**1**, where leveling occurs at −40 and −10 °C, respectively, with convergence at *k ca.* 1.2×10^7 s^{-1}.[4b] Note, in both cases, that Arrhenius curvature begins at a higher temperature for the [α,α-$^2H_2$] carbene.

At 25 °C, the global rate constant for decay of **2** is 2.4×10^7 s^{-1}, which can be partitioned as 1.8×10^7 s^{-1} for H-shift to **4**/**5**, 1.4×10^6 s^{-1} for 1,2-mesityl shift to **6**, and 4.8×10^6 s^{-1} for insertion to **7**. For [$^2H_2$]-**2**, the corresponding total rate constant is 8.2×10^6 s^{-1}, and the partitioned rate constants are 3.7×10^6 s^{-1} (1,2-D shift), 1.0×10^6 s^{-1} (1,2-mesityl shift), and 3.4×10^6 s^{-1} (insertion). The global rate constants are somewhat smaller than those reported for **1** (6.2×10^7 s^{-1}) and [$^2H_2$]-**1** (2.1×10^7 s^{-1}) at 25 °C.[4b]

Our partitioned rate constants afford a large KIE for 1,2-H or 1,2-D shifts of **2** at 25 °C; k_H/k_D = 4.8. Product distributions were not corrected for incursion of **3*** at other temperatures, so that those global rate constants cannot be accurately partitioned to reflect carbene-only product formation. From the global rate constants for decay of **2** or [$^2H_2$]-**2** (Fig. 1), k_H/k_D appears to decrease with decreasing temperature, as was reported for **1**.[4b] As shown below, however, this picture is deceptive.

Thus far, the chemistry of mesitylmethylchlorocarbene closely parallels that of benzylchlorocarbene.[1a,2,4a,b] An important divergence occurs, however, for product formation at low temperature. Photolyses of **3** and [$^2H_2$]-**3** were carried out at 30, 0, −35 and −70 °C. At the two higher temperatures, **4–7** accounted for > 96% of the products from either **2** or [$^2H_2$]-**2**. However, at −35 or −70 °C, product mixtures became increasingly complex, with up to six new products formed. Of these, we have identified **8–11**.

$\text{MesC}{\equiv}\text{CH}$ **8** $\text{MesCH}_2\text{CHCl}_2$ **9** $\text{MesCH}_2\text{CCl}{=}\text{CClCH}_2\text{Mes}$ **10**

$\text{MesCH}_2\text{CCl}{=}\text{N}{-}\text{N}{=}\text{CClCH}_2\text{Mes}$ **11**

Acetylene **8**, also present in 2% yield in the 25 °C photolysis of **3**, appears to be an elimination product of **4**, **5** or **6**. Dichloride **9** results from reaction of **2** with HCl. The chromatographically inseparable mixture of 15 : 85 carbene dimer **10** and azine **11** (from **2** + **3**) was identified by NMR, GC–MS, microanalysis and exact mass measurements. Yields of **8** and **9** were low (⩽2%) under all conditions; whereas (**10** + **11**) constituted 2.5 and 11.2% of the products at −35 and −70 °C, respectively. For [$^2H_2$]-**2**, dimer/azine formation was already apparent at 0 °C (2.1%), and increased to 8.5 and 16% at −35 and −70 °C. Analogous azine formation has also been observed from benzylfluorodiazirine and benzylfluorocarbene.[8]

Azine formation was discounted as a complicating factor in the chemistry of carbene **1**,[4b] but it cannot be ignored here. Moreover, azine formation will be more marked, and commence at higher temperatures with [$^2H_2$]-**2**, which has a threefold lower rate constant for decay at 25 °C than does **2**; intramolecular reactions compete less efficiently with intermolecular reactions for the deuteriated carbene.

Azine (and dimer) formation are initially observed for **2** at −35 °C and for [$^2H_2$]-**2** at 0 °C. Arrhenius curvature (Fig. 1) becomes apparent at similar temperatures (−40 and −20 °C). These correspondences are not coincidental; with decreasing temperature the intramolecular reactions of the carbenes are slowed sufficiently so that the effectively temperature independent intermolecular azine formation gains in importance, causing significant curvature and levelling in the Arrhenius correlations. Consistent with this explanation, we find that twofold dilution of diazirines **3** and [$^2H_2$]-**3** (A_{342} = 0.5 in isooctane, [diazirine] *ca.* 0.01 mol dm^{-3}) leads to Arrhenius correlations for both carbenes that are linear to −70 °C (inset, Fig. 1).

These new correlations afford E_a = 4.8 kcal mol^{-1} (1 cal = 4.184 J), log *A* = 10.7 s^{-1} and $\Delta S^*(298)$ = −11.4 e.u. for **2**, and analogous values of 4.6 kcal mol^{-1}, 10.2 s^{-1} and −13.7 e.u. for [$^2H_2$]-**2**. Of course, these data contain contributions from all carbene decay channels, but they are similar to the activation parameters determined for carbene **1**.[4b] Importantly, with the disappearance of Arrhenius curvature, the temperature dependence of the KIE for **2**/[$^2H_2$]-**2** no longer exhibits a marked decrease with decreasing temperature. It is also interesting to note from the activation parameters that k_H/k_D for the disappearance of **2**/[$^2H_2$]-**2** (at least from the global rate constants) is controlled by entropic, not enthalpic factors.

In the cases of **1** and [$^2H_2$]-**1**, Arrhenius curvature was attributed to increasing intervention of carbenic reaction with the isooctane solvent and/or 1,2-H shift tunnelling.[4b] However, no products of carbene/isooctane reactions were observed.[4b] Moreover, in preliminary experiments, we have observed the formation of azine (up to 30%) in photolyses of benzylchlorodiazirine (A_{344} = 0.7) at −70 °C in isooctane, under conditions analogous to those used in the photolysis of **3**. In the light of our findings with carbene **2**, it seems likely that azine formation is a major cause of the Arrhenius curvature observed in the H-shift reactions of **1**.

We do not exclude tunnelling as a contributory factor to the Arrhenius curvature. Tunnelling is surely involved in the rearrangements of **1** in argon matrices at 20–30 K,[4a] and may be important in the rearrangements of CH_3CCl and CD_3CCl at temperatures that are much closer to ambient.[4c,d]

In conclusion, the intramolecular chemistry of mesitylmethylchlorocarbene parallels that of benzylchlorocarbene, but the increasing product complexity and azine formation at low temperatures suggest important revisions to previous interpretations of the rearrangement kinetics of the latter carbene. We are continuing our studies of carbenes **1**, **2** and their fluoro analogues.

We are grateful to the National Science Foundation for financial support, to Professors J. L. Goodman, M. T. H. Liu and M. S. Platz for helpful discussions, and to Dr L. Maksimovic for technical assistance.

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Received, 4th November 1996; Com. 6/07552E