The Gas-Phase Reaction of Methylene-*t* with Ethylene

Sir:

Several series of experiments have demonstrated that methylene reacts in the gas phase with ethylene to form both cyclopropane and propylene in amounts variable with the pressure of the system.[1,2] The quantitative mechanistic explanations of these data have been the subject of considerable discussion, involving both the methylene reactions themselves[3] and the isomerization of cyclopropane to propylene.[4] Despite general agreement concerning the qualitative experimental facts, several areas of uncertainty, which can be clarified through tracer investigations, still exist.

We have studied the reactions of CHT with ethylene in the pressure range of 1 to 3000 cm, and have measured two parameters for each experiment: (a) f_Δ, the yield of cyclopropane-*t* relative to the sum of cyclopropane-*t* and propylene-*t;* and (b) f_a, the fraction of propylene-*t* with tritium in the alkyl position,[5] *i.e.*, $CH_2TCH{=}CH_2$. Since previous experiments have relied almost entirely on measurements of f_Δ as a function of pressure, the additional measurement of f_a permits critical evaluation of earlier mechanistic suggestions. Our procedure has utilized CHT from the 3120-A photolysis of CHT=CO, and the experiments have included samples both with and without O_2 present during photolysis.

The most important experimental observations are: (a) the values for f_Δ range from 0.001 at 1 cm to 0.78 ± 0.03 at 3000 cm, in reasonable agreement with previous $CH_2 + C_2H_4$ experiments; (b) the value of f_a in the absence of O_2 increases from 0.51 ± 0.02 to 0.86 ± 0.02 over the same range of increasing pressure; (c) the value of f_a in O_2-scavenger experiments has a low-pressure limit of 0.58 ± 0.02 and also increases with pressure; (d) at a given pressure, the value of f_Δ is *lowered* by the inclusion of O_2 in the system, *i.e.*, the primary effect of O_2 is the suppression of a reaction which leads predominantly to the formation of cyclopropane-*t*.

These data are quantitatively consistent with three primary reaction paths for CHT: (1) 17 ± 2% reacting as ^{1}CHT by insertion into the C–H bond of C_2H_4, with the formation of $CH_2TCH{=}CH_2$; (2) 54 ± 3% reacting as ^{1}CHT with the double bond to form cyclopropane-*t;* and (3) 29 ± 3% reacting as ^{3}CHT with C_2H_4 to form triplet $\cdot CHTCH_2CH_2\cdot$, which ring-closes to form cyclopropane-*t;* together with (4) the secondary isomerization of cyclopropane-*t* from (2) or (3) to propylene-*t*, unless first stabilized by collision. No assumption of a pressure dependence of the ^{3}CHT fraction is required, although a small variation in this fraction might not be inconsistent with the observations.[6]

The assignment of multiplicity is based on the assumption that O_2 entirely suppresses the formation of cyclopropane-*t* by reaction 3. Previous investigations have placed limits of ~5[7] and ~2%[8] oxygen as the necessary amount to scavenge effectively triplet products in other ketene–olefin experiments. Our results with *trans*-2-butene indicate that the oxygen reaction is much more efficient, showing no variation in product distribution between 0.03 and 3% O_2 concentration. Scavenger oxygen is consumed during the photolysis of ketene, and our experiments with very low O_2 concentrations have been possible because of the tracer nature of our product measurement. The previous limits reflect only the amount of O_2 necessary to ensure its presence at the end of an experiment. The present ethylene experiments contained 2–3% oxygen in 30–100:1 ethylene–ketene mixtures with an upper limit on ketene conversion to products of ~5%. Any interaction of singlet methylene with oxygen[8] will not alter the conclusions drawn from these experiments, since the measurements are concerned with the relative amounts following competitive reaction paths.

From the pressures at which one-half of the molecules are collisionally stabilized, estimates of the average excitation energy of cyclopropane-*t* can be made by RRKM treatment: 105 kcal/mole ($p_{1/2} \sim 250$ cm) for reaction 2 and 85 kcal/mole ($p_{1/2} \sim 25$ cm) for reaction 3. The lower value of the latter accounts for the decrease in f_Δ with inclusion of O_2 and indicates a loss of the excitation energy from CHT addition of C_2H_4 prior to the ring-closing step. This assumption of deexcitation prior to ring closure implies that 85 kcal/mole is the exothermicity of the ring-closing step, and therefore that $\Delta H_f{}^3(\cdot CHTCH_2CH_2\cdot)$ is ~97 kcal/mole.[9]

The propylene-*t* from the isomerization of cyclopropane-*t* is a mixture of all of the possible isotopic isomers, and, taken alone, would give a value of f_a = 0.42 ± 0.02.[10] The low-pressure values of f_a represent the sum of the direct insertion reaction ($f_a = 1.00$) and of the contributions from reaction 2 or 2 + 3, respectively, for experiments with and without O_2. We do not yet have definitive experiments in this system to indicate what fraction of the suppression of reaction 3 by O_2 occurs with ^{3}CHT *vs.* that with $^3\cdot CHTCH_2CH_2\cdot$. However, in similar reactions of ^{3}CHT with *trans*-2-butene, the O_2 reaction largely occurs with the C_5 diradical.[11] Since the rate of ^{3}CHT reaction with O_2 must be similar in C_2H_4 and C_4H_8, we conclude that the triplet trimethylene-*t* is being effectively scavenged by reaction with O_2. Furthermore, the diradical must

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(1) (a) G. B. Kistiakowsky and K. Sauer, *J. Am. Chem. Soc.*, **78**, 5699 (1956); (b) H. M. Frey, *ibid.*, **79**, 1259 (1957); (c) H. M. Frey and G. B. Kistiakowsky, **79**, 6373 (1957).

(2) (a) B. S. Rabinovitch, E. Tschuikow-Roux, and E. W. Schlag, *ibid.*, **81**, 1081 (1959); (b) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962); (c) D. W. Setser, B. S. Rabinovitch, and J. W. Simons, *J. Chem. Phys.*, 40, 1751 (1964); (d) D. W. Setser, B. S. Rabinovitch, and J. W. Simons, *ibid.*, **41**, 800 (1964).

(3) Recent review articles include: (a) H. M. Frey, *Progr. Reaction Kinetics*, **2**, 131 (1964); (b) W. B. DeMore and S. W. Benson, *Advan. Photochem.*, **2**, 219 (1964); (c) H. M. Frey in "Carbene Chemistry," W. Kirmse, Ed., Academic Press Inc., New York, N.Y., 1964, p 217.

(4) *Cf.* (a) F. T. Smith, *J. Chem. Phys.*, **29**, 235 (1958); (b) D. W. Setser and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **86**, 564 (1964); (c) S. W. Benson and P. S. Nangia, *J. Chem. Phys.*, **38**, 18, 1963).

(5) Chromatographic details are given by: E. K. C. Lee and F. S. Rowland, *Anal. Chem.*, **36**, 2181 (1964); E. K. C. Lee, J. W. Root, and F. S. Rowland, "Chemical Effects of Nuclear Transformations," Vol. I, International Atomic Energy Agency, Vienna, 1965, p 55.

(6) See, for example, B. S. Rabinovitch, K. W. Watkins, and D. F. Ring, *J. Am. Chem. Soc.*, **87**, 4961 (1965).

(7) (a) J. W. Simons and B. S. Rabinovitch, *J. Phys. Chem.*, **68**, 1322 (1964); (b) F. H. Dorer and B. S. Rabinovitch, *ibid.*, **69**, 1964 (1965).

(8) R. W. Carr, Jr., and G. B. Kistiakowsky, *ibid.*, 70, 118 (1966).

(9) See B. C. Roquitte, *ibid.*, 70, 1334 (1966).

(10) Deviation of this value from the statistical value of f_a = 0.50 for the fraction of hydrogen atoms in alkyl positions occurs because of the primary isotope effect in the transfer of tritium during the isomerization of cyclopropane. The data of R. Weston, *J. Chem. Phys.*, **26**, **975** (1957), on the thermal isomerization of cyclopropane-*t* (k_H/k_T = 3.7 at 492°) yield an expected value of f_a = 0.43.

(11) C. McKnight and F. S. Rowland, *J. Am. Chem. Soc.*, **88**, 3179 (1966).

survive long enough for collision and reaction with O_2 to dominate over rearrangement, and requires a radical lifetime $\geq 10^{-8}$ sec. A lifetime of $10^{-10.5}$ sec has been calculated for singlet trimethylene from the thermal isomerization of cyclopropane at 445°.[4c]

Earlier experiments conducted with ketene and ethylene in the presence of excess CO_2 indicated that cyclopropane:propylene ratios of 1.0 could be obtained at much lower pressures than that required for ketene–ethylene alone,[1c] and have been interpreted as resulting from very efficient collisional deexcitation of cyclopropane in the presence of CO_2. We have also observed relatively high values of f_Δ in our experiments ($f_\Delta = 0.83$ at 200 cm) with CO_2, but the tritium distribution ($f_a = 0.50 \pm 0.03$) indicates that the residual propylene-*t* has passed through a randomizing intermediate. These results are consistent with collisional conversion of ^{1}CHT to ^{3}CHT, followed by triplet reaction through the trimethylene-*t* intermediate, with only a small fraction of ^{1}CHT reaction in the system.

The ratio of insertion of ^{1}CHT into the C–H bond *vs.* reaction with the C=C bond is 0.08 ± 0.01 per bond. Previous estimates of a lower ratio (in the $^1CH_2$ system) have not taken the $^3CH_2$ contribution into account, as has been discussed earlier.[7]

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(3)-1,2-Dicarbollyl Complexes of Nickel(III) and Nickel(IV)

Sir:

We wish to report a new preparation of the (3)-1,2-dicarbollyl[1] sandwich complexes of iron[1-3] and cobalt,[4] $M^{n+}(B_9C_2H_{11})_2^{n-4}$ (M = Fe, Co). In addition, this preparative method has been employed in the preparation of similar species which contain nickel in the formal oxidation state of 2+, 3+, and 4+.

The $B_9C_2H_{12}^-$ ion, derived from 1,2-dicarbaclovododecaborane(12),[5] in hot aqueous sodium hydroxide solution (~40% by weight) was allowed to react with MCl_2 salts (M = Fe, Co, or Ni) to produce the complexes $Fe(B_9C_2H_{11})_2^{2-}$, $Co(B_9C_2H_{11})_2^-$, and $Ni(B_9C_2H_{11})_2^{2-}$, respectively. This preparation appears to involve the intermediate formation of the (3)-1,2-dicarbollide ion[1] by means of the following equilibrium.

$$B_9C_2H_{12}^- + OH^- \rightleftharpoons B_9C_2H_{11}^{2-} + H_2O$$

The $B_9C_2H_{11}^{2-}$ ion, generated *in situ*, may then react with the metal salts.[6] The M^{II} derivatives of iron and nickel were readily oxidized by air to the corresponding M^{III} species, while the Co^{II} complex disproportionated to form the Co^{III} complex and cobalt metal. All three M^{III} derivatives were isolated as their tetramethylammonium salts in up to 86% yield.

The $Fe^{III}(B_9C_2H_{11})_2^-$ and the $Co^{III}(B_9C_2H_{11})_2^-$ have been described previously.[2,4] Salts of newly discovered $Ni^{III}(B_9C_2H_{11})_2^-$ (I) are stable, brown [λ_{max} (ϵ): 237 (8500), 337 (21,000), and 435 (sh) mμ (3600)], and paramagnetic (μ_{eff} = 1.56 BM). *Anal.* Calcd for $(CH_3)_4NNi(B_9C_2H_{11})_2$: C, 24.14; H, 8.62; B, 48.97; N, 3.52; Ni, 14.76; formula wt, 398. Found: C, 24.02; H, 8.68; B, 49.35; N, 3.78; Ni, 14.48; formula wt, 399 (osmometric). I may be viewed as the (3)-1,2-dicarbollyl analog of nickelicinium ion. The oxidation of I in aqueous solution to the neutral species, $Ni^{IV}(B_9C_2H_{11})_2$ (II), required 1 equiv of $FeCl_3$. II is a diamagnetic yellow crystalline solid [λ_{max} (ϵ): 293 (18,000) and 425 mμ (1200)] which is stable in air, soluble in most organic solvents including saturated hydrocarbons, and sublimes *in vacuo* at 150°. *Anal.* Calcd for $Ni(B_9C_2H_{11})_2$: C, 14.83; H, 6.85; B, 60.18; Ni, 18.14; mol wt, 323. Found: C, 15.13; H, 6.85; B, 60.33; Ni, 17.84; mol wt, 309 (osmometric). High-resolution mass spectroscopy unequivocally verified the formulation $NiB_{18}C_4H_{22}$: calcd for $^{62}Ni^{11}B_{18}{}^{12}C_4{}^{1}H_{22}$, 330.268; found: 330.270. The ^{1}H nmr spectrum of II in benzene contained only a single resonance at τ 6.86 which was attributed to the carborane protons. The ^{11}B nmr spectrum of II closely resembled that of the isoelectronic $Co^{III}(B_9C_2H_{11})_2^-$ and $Fe^{II}(B_9C_2H_{11})_2^{2-}$. Polarography of II gave two reversible one-electron reductions at potentials +0.22 and − 0.63 v *vs.* sce. One equivalent of cadmium metal quantitatively reduced II to I while stronger reducing agents, *e.g.*, sodium amalgam, were required to convert I to $Ni^{II}(B_9C_2H_{11})_2^{2-}$. These data strongly support our formulation of I and II as Ni^{III} and Ni^{IV} complexes, respectively.

At the present time, very few well-characterized Ni^{III} and Ni^{IV} compounds have been described,[7a,b] and these species may be roughly divided into three classes. One class comprises the complex oxides and fluorides, and a second class contains complexes with bidentate ligands which employ phosphorus, arsenic, sulfur, or nitrogen as donor stoms.[8] Finally, the third class is exemplified by the $Ni^{III}(C_5H_5)_2^+$ (nickelicinium) ion[9] which resists oxidation[10] to the dipositive complex, $Ni^{IV}(C_5H_5)_2^{2+}$. The new Ni^{III} and Ni^{IV} complexes described in this communication appear to fall in the third class and may have the sandwich structure of the other known (3)-1,2-dicarbollyl complexes.

The chemistry and structures associated with the nickel system are currently under investigation, and the results of these studies will be reported in full at a later data.

(1) M. F. Hawthorne and R. L. Pilling, *J. Am. Chem. Soc.*, **87**, 3987 (1965), present the nomenclature system employed for these species and the $B_9C_2H_{11}^{2-}$ dicarbollide ions.

(2) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *ibid.*, **87**, 1818 (1965).

(3) A. Zalkin, D. H. Templeton, and T. E. Hopkins, *ibid.*, **87**, 3988 (1965).

(4) M. F. Hawthorne and T. D. Andrews, *Chem. Commun*, 443 (1965).

(5) R. A. Wiesboeck and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 1642 (1964).

(6) The possibility exists that the $B_9C_2H_{12}^-$ ion actually complexes with the metal ion in the first step of the reaction followed by proton abstraction by OH^- in a subsequent step.

(7) (a) For a review on the subject, see R. S. Nynolm, *Chem. Rev.*, **53**, 263 (1953), and references therein; (b) B. N. Figgis and J. Lewis [*Progr. Inor. Chem.*, **6**, 195 (1964)] discuss magnetic properties.

(8) As an example, see E. I. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 3016 (1965), for a recent series of references.

(9) G. Wilkinson, P. L. Pauson, J. M. Birmingham, and F. A. Cotton, *ibid.*, **75**, 1011 (1953).

(10) G. Wilkinson, P. L. Pauson, and F. A. Cotton, *ibid.*, **76**, 1970 (1954).