1.4348). Glpc (General Electric Co. XF 1150) showed the presence of a single component with the same retention time as Me_2CHCH_2Br: nmr (in CCl_4) δ 1.08 (s, 6 H, Me_2C), 3.23 ppm (s, 2 H, CH_2Br), as expected for Me_2CDCH_2Br; ir (neat) 2972 s, 2940 s, 2879 m, 2154 w (ν_{C-D}), 1470 s, 1439 m, 1390 m, 1374 m, 1323 w, 1295 w, 1256 s, 1244 s, 1238 sh, 1208 m, 1157 w, 1133 w, 1108 w, 974 w, 934 m, 970 m, 809 m, 798 w, and 651 s cm^{-1}.

(b) Preparation of $Me_3SiCH_2CDMe_2$. The Grignard reagent was prepared from 15.6 g (0.113 mol) of Me_2CDCH_2Br and 5.40 g (0.225 g-atom) of magnesium turnings in diethyl ether. Trimethylchlorosilane (11.9 g, 0.225 mol) in ether was added and the reaction mixture was stirred and heated at reflux for 72 hr. Hydrolysis with saturated ammonium chloride solution was followed by distillation of the dried organic layer to give 10.2 g (71%) of the product, bp 106–108°, $n^{25}D$ 1.3994. The bp of $Me_2CHCH_2SiMe_3$ prepared in this study was 106.5–108° and the $n^{25}D$ was 1.3988. The glpc retention time of the product on an XF-1150 column was identical with that of the undeuterated material; nmr (in CCl_4) −0.07 (s, 9 H, Me_3Si), 0.48 (s with further minor splitting, 2 H, CH_2Si), 0.88 (s, with further minor splitting, 6 H, Me_2C). The more complex patterns presumably are a consequence of preferred conformations. The infrared spectrum showed C–D bands at 2161 and 2135 cm^{-1}.

A deuterium analysis by the falling drop method (J. Nemeth) showed 5.40 atom % excess deuterium, equivalent to 97% replacement of one hydrogen by deuterium. Assuming that isotopic rearrangement has not occurred during the Grignard reaction, it appears reasonable to conclude that the deuterium is located almost exclusively in the β position, *i.e.*, the product is $Me_3SiCH_2CDMe_2$.

(c) The Insertion Reaction. The reaction with $PhHgCCl_2Br$ was carried out in the usual manner with 30 mmol of the silane and 10 mmol of the mercurial. The product was obtained in 36% yield, $n^{25}D$ 1.4631. The glpc retention time was identical with that of $Me_3SiCH_2C(CCl_2H)Me_2$.

Deuterium analysis by the falling drop method showed 5.35 atom % excess deuterium in the product, equivalent to 96% replacement of one hydrogen by deuterium: nmr (in CCl_4) δ 0.03 (s, 9 H, Me_3Si), 0.88 (s, 2 H, $SiCH_2$), 1.10 ppm (s, 6 H, Me_2C). A high amplitude scan revealed a very weak signal at 5.45 ppm, the position of the CCl_2H proton in the undeuterated product; ir (neat) 2960 s (broad), 2905 s, 2886 sh, 2809 sh, 2220 w (ν_{C-D}), 1940 w, 1855 w, 1555 w, 1478 m, 1469 m, 1425 m, 1391 m, 1375 m, 1296 m, 1258 s, 1228 m, 1205 w, 1155 w, 1096 w, 1085 w, 1015 m, 980 m, 967 m, 919 m, 849 s, 785 s, 769 s, 743 m, 709 m, and 697 m cm^{-1}.

In a similar experiment the unconverted starting silane was recovered and analyzed for deuterium. It was found to contain 5.47 atom % excess deuterium, equivalent to 99% replacement of one hydrogen by deuterium.

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Radiation-Induced Cationic Chain Formation of Ether from Isopropyl Alcohol Vapor[1]

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Contribution from the Chemistry Department, University of Alberta, Edmonton 7, Canada. *Received December 29, 1969*

Abstract: During the γ radiolysis of isopropyl alcohol vapor at temperatures above 250°, diisopropyl ether is produced by a cationic chain mechanism. The mechanism is zero order with respect to alcohol pressure and has an activation energy of 40 ± 1 kcal/mol independent of pressure over the range studied (100–2000 Torr). The ether yield decreases with increasing dose and is not dependent on the surface:volume ratio of the reaction vessel. At 350°, 100 Torr and 2.9×10^{17} eV/g, G(ether) = 1000; the G value is inversely proportional to the alcohol pressure. The addition of about 10 mol % of the following additives decreased the ether yield by amounts in the following increasing order: water < propylene < sulfur hexafluoride < acetone < ammonia. The proton affinities of the additives increase in the same order. The chain propagation reactions appear to be $(ProH)_mH^+ \rightarrow Pr_2O \cdot H^+ \cdot (OH_2) (Pr_2OH_{m-2}$ (4_m), $Pr_2O \cdot H^+ \cdot (OH_2)(PrOH)_{m-2} + 2PrOH \rightarrow Pr_2O + H_2O + (PrOH)_mH^+$ (5_m). The presence of a foreign (nonalcohol) molecule in the "clustered" ion apparently inhibits reaction 4_m. The addition of >10% propylene to the alcohol sensitizes ether formation, presumably by way of the exothermic reaction $C_3H_6^+ + PrOH \rightarrow C_3H_5 + PrOH_2^+$ (eq 9).

A cationic chain reaction that forms diethyl ether from ethanol during vapor phase radiolysis at elevated temperatures has recently been discovered.[2] We have extended the study of this type of reaction by investigating the formation of diisopropyl ether during the radiolysis of isopropyl alcohol vapor at temperatures between 125 and 406°.

Experimental Section

Materials. "Chromatoquality" isopropyl alcohol from Matheson Coleman and Bell was purified by adding 3 g of dinitrophenylhydrazine and 1 ml of concentrated sulfuric acid to 2 l. of the alcohol and refluxing the solution in a stream of dry nitrogen for 3 hr. The isopropyl alcohol was then fractionally distilled and the middle fraction was collected. Although this treatment decreased the small amounts of aldehydes and ketones in the alcohol, it formed a substantial amount of ether. As the study of the radiation-induced formation of ether was the objective of this investigation, the ether had to be removed from the alcohol before irradiation. This was done by fractional distillation of the previously treated alcohol in a spinning band column, with a reflux ratio of 20:1. The middle fraction of the distillate contained $< 2 \times 10^{-6}$ M ether. This isopropyl alcohol was then degassed and stored under vacuum in a Pyrex reservoir.

Ammonia (Canadian Industries Ltd.), propylene (Phillips Research Grade), sulfur hexafluoride (Matheson Co.) and acetone (Shawinigan, Reagent) were degassed and stored under vacuum in Pyrex vessels.

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[1] This work received financial assistance from the National Research Council of Canada.

[2] K. M. Bansal and G. R. Freeman, *J. Amer. Chem. Soc.*, **90**, 5632 (1968).

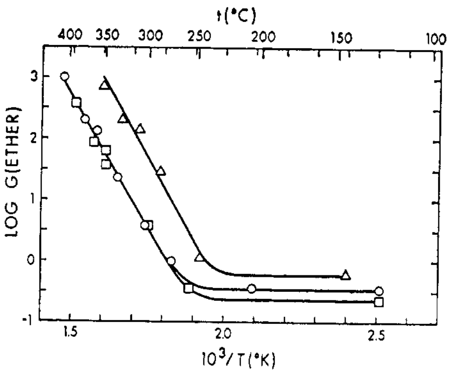

Figure 1. Arrhenius plots of G(ether) at different isopropyl alcohol vapor densities: △, 0.156 g/l., 3.1×10^{18} eV/g; ○, 0.78 g/l., 3.2×10^{19} eV/g; □, 3.12 g/l., 3.1×10^{18} eV/g. These correspond to alcohol pressures of about 100, 500, and 2000 Torr at 350°.

Sample Handling. The preparation and treatment of samples before and after irradiation was the same as that described earlier for ethanol samples.[3]

The irradiation dose rate in isopropyl alcohol was calculated from that in ethanol,[3] correcting for the difference in electron density and the decay of the ^{60}Co source. The dose rate was 3.5×10^{19} eV/g hr.

The value of the surface:volume ratio of the irradiation cells was varied by packing the usual 500-ml Pyrex vessels with small glass tubes (6 mm OD × 25 mm). The surface area was calculated and the net volume of the cell was measured.

The samples were analyzed by gas chromatography, using a 12 ft × $^3/_{16}$ in. glass column packed with 10% Carbowax 1540 on Chromosorb WAW, and a flame ionization detector.

Results

Effect of Temperature at Constant Isopropyl Alcohol Density. The yield of diisopropyl ether was measured at temperatures between 125 and 406° at isopropyl alcohol densities of 0.156, 0.78, and 3.12 g/l. which correspond to pressures in the vicinities of 100, 500, and 2000 Torr, respectively. Arrhenius plots of the results are shown in Figure 1. The values of G(ether) were independent of temperature below about 225° and decreased somewhat with increasing alcohol density: G(ether) was 0.6, 0.35, and 0.23 at 0.156, 0.78, and 3.12 g/l., respectively. At temperatures above about 250° a chain reaction occurred with an overall activation energy of 40 ± 1 kcal/mol, independent of alcohol density over the range studied (Figure 1). Values of G(ether) up to 1030 were measured.

The curves for the densities 0.78 and 3.12 g/l. coincide at the higher temperatures because of the fortuitous cancellation of dose and density effects. The value of G(ether) tends to decrease with increasing dose and with increasing pressure (see later); the 0.78 g/l. samples were given a dose of 3.2×10^{19} eV/g, whereas the 3.12 g/l. samples were given 3.1×10^{18} eV/g.

"Blank" samples were run for all the irradiation conditions used. These samples were prepared, put through the heating cycle, and analyzed in the same way as the irradiated samples, but they received no irradiation. In all cases the amount of ether formed was less than 1%, and often less than 0.1%, of that formed in the corresponding irradiated sample.

Effect of Isopropyl Alcohol Pressure (Density) at Constant Temperature. The yield of ether was measured as a function of alcohol pressure at two different temperatures (325 and 350°) and two different irradiation doses (2.9×10^{17} and 3.2×10^{18} eV/g). The pressures ranged from about 100 to 2000 Torr (0.156–3.12 g/l.). The yield decreased with increasing pressure, and the slope of the log–log plot of G(ether) against alcohol pressure was −1.0 in each case (Figure 2).

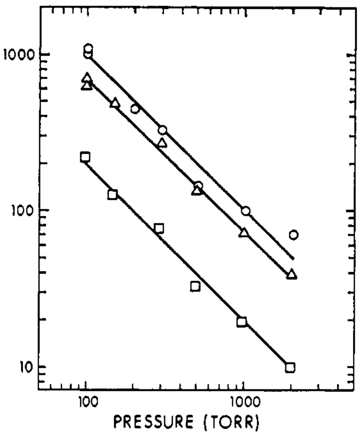

Figure 2. Effect of isopropyl alcohol pressure on the ether yield: temperature, ○, △, 350°; □, 325°; dose (eV/g), ○, 2.9×10^{17}; △, □, 3.2×10^{18}.

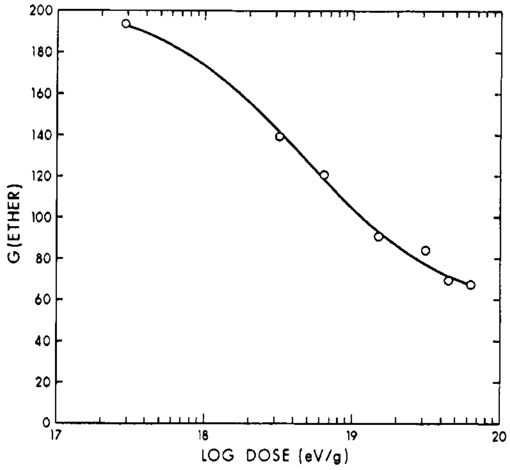

Figure 3. Ether yield as a function of irradiation dose at 350° and 508 Torr (0.78 g/l.).

"Blank" samples were put through the heating cycle to 350° at different alcohol pressures, but were not irradiated. The amount of ether formed was 3% of the radiolysis yield at 2000 Torr and even more negligible at lower pressures.

Effect of Irradiation Dose at 350°. At an alcohol pressure of 508 Torr (0.78 g/l.) the dose was increased from 2.9×10^{17} to 6.3×10^{19} eV/g, and the value of G(ether) decreased from 198 to 67 (Figure 3).

Similarly, at an isopropyl alcohol pressure of 100 Torr G(ether) decreased from 1020 at 2.8×10^{17} eV/g to 600 at 3.1×10^{18} eV/g.

Effects of Additives at 350°. Each of the following compounds was added to 100 Torr of isopropyl alcohol to determine its effect on the yield of diisopropyl ether: propylene, acetone, water, ammonia, and sulfur hexafluoride. The 100-eV yields of ether are reported in two ways in Table I: (i) g(ether) is based on the en-

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(3) K. M. Bansal and G. R. Freeman, *J. Amer. Chem. Soc.*, **90**, 7183 (1968).

Table I. Effects of Additives on the Yield of Isopropyl Ether[a]

Additive	Mol %	g(ether)[b]	G(ether)[c]
None		666	666
C_3H_6	10.3	370	344
	17.9	430	371
	50.6	725	418
$(CH_3)_2CO$	0.9	485	480
	9.0	86	78
H_2O	1.1	520	518
	13.0	567	543
NH_3	15.0	<6	<6
SF_6	10.3	275	223

[a] t = 350°; alcohol pressure = 100 Torr, dose = 3.1×10^{18} eV/g. [b] g(ether) was calculated from the energy initially absorbed only in the alcohol. [c] G(ether) was calculated from the total energy absorbed by the gas mixture.

ergy absorbed by the alcohol; (ii) G(ether) is based on the total energy absorbed by the gas mixture.

The value of g(ether) decreased when 10 mol % of propylene was added, but increased again as more propylene was introduced. The value of G(ether) changed in a similar way, but the rate of increase at high propylene pressures was relatively small (Figure 4).

The ether yield was decreased somewhat by each of the additives used. Judging from the values of G(ether) at 10 mol % additive, the order of increasing effectiveness as an inhibitor was water < propylene < sulfur hexafluoride < acetone < ammonia (Table I).

Effect of Surface : Volume Ratio of the Reaction Vessel on G(ether). To determine whether wall reactions play an important role in the mechanism of ether formation at 350°, the surface:volume ratio of the irradiation cell was changed over a sixfold range. A constant amount, 0.078 g, of alcohol was used in each experiment. The surface:volume ratio was increased by packing the vessel with pieces of glass tubing, so the net gas volume of the vessel decreased. The alcohol pressure therefore increased somewhat with increasing surface: volume.

The results are listed in Table II. The values in the last two columns show that the changing ether yield was due to the changing alcohol pressure, not to the changing surface:volume ratio. It is therefore concluded that wall reactions do not contribute appreciably to ether formation.

Table II. Effect of Surface : Volume Ratio on Ether Yield at 350°

$P_{alcohol}$, Torr	Net vol, cm^3	Surface: volume, cm^{-1}	G-(ether)$_{obsd}$[a]	G-(ether)$_P$[b]
103	490	0.77	625	660
126	400	2.3	530	540
151	335	4.4	450	457

[a] Observed ether yield in the vessel with the listed ratio of surface: volume. Dose = 3.2×10^{18} eV/g. [b] Ether yield obtained at pressure $P_{alcohol}$ in a vessel with surface:volume ratio = 0.77. These yields were taken from the middle curve in Figure 2.

Discussion

Mechanism. The results are consistent with a reaction mechanism analogous to that proposed for the formation of diethyl ether during the radiolysis of ethanol vapor at high temperatures.[4] The main portion of the mechanism will therefore be presented first and the results will be discussed in terms of it.

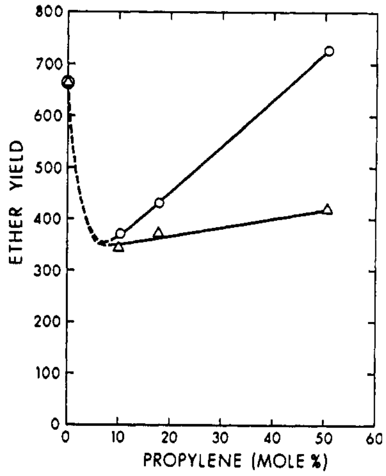

Figure 4. Effect of propylene on the ether yield at 350° and 100 Torr of isopropyl alcohol: dose = 3.1×10^{18} eV/g; ○, g(ether), calculated on the basis of the energy initially absorbed only in the alcohol; Δ, G(ether), calculated on the basis of the total energy absorbed by the alcohol and propylene.

$$PrOH \rightsquigarrow PrOH^+ + e^- \tag{1}$$

$$PrOH^+ + PrOH \longrightarrow PrOH_2^+ + (CH_3)_2COH \tag{2}$$

$$PrOH_2^+ + PrOH \rightleftharpoons (PrOH)_2H^+ \tag{3$_1$}$$

$$(PrOH)_2H^+ + PrOH \rightleftharpoons (PrOH)_3H^+ \tag{3$_2$}$$

$$(PrOH)_mH^+ + PrOH \rightleftharpoons (PrOH)_{m+1}H^+ \tag{3$_m$}$$

$$(PrOH)_mH^+ \longrightarrow Pr_2OH^+(OH_2)(PrOH)_{m-2} \tag{4$_m$}$$

$$Pr_2OH^+(OH_2)(PrOH)_{m-2} + 2PrOH \longrightarrow Pr_2O + H_2O + (PrOH)_mH^+ \tag{5$_m$}$$

$$(PrOH)_mH^+ + e^- \longrightarrow \text{neutralization} \tag{6$_m$}$$

The minimum value of m required in reactions 4_m and 5_m is two. Equation 5_m occurs in several steps involving the successive growth of the clustered ion by alcohol molecule attachment and partial dissociation by the more or less random detachment of one of the molecules from the cluster. For reasons stated earlier,[4] reaction 5_m is approximately thermoneutral, and the heat of eq 4_m should be about equal to that of eq 7;

$$2PrOH \longrightarrow Pr_2O + H_2O \tag{7}$$

it can be assumed that $\Delta H_7 \approx -5$ kcal/mol, since the analogous reactions of methanol and ethanol are each exothermic by 6 kcal/mol and the cross reaction between methanol and t-butyl alcohol is exothermic by 5 kcal/mol.[5]

The observation of values of G(ether) up to 1000 requires interpretation in terms of a chain mechanism, such as the one above.

Effects of Additives. Each of the additives used, at a concentration of about 10 mol %, inhibited the formation of ether to a certain extent (Table I). The amount of inhibition caused by additive increased with increasing proton affinity of the additive (Table III). A high proton affinity enhances the tendency of a

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(4) K. M. Bansal and G. R. Freeman, *J. Amer. Chem. Soc.*, **92**, 4173 (1970).

(5) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

molecule to be part of the "solvation" cluster of the cation. The presence of a foreign molecule in the cluster apparently inhibits reaction 4_m.

Table III. Correlation of Inhibitor Effectiveness with Proton Affinity

Additive	Mol, %	*PA*, kcal/mol[a]	*G*(ether)[b]
None			666
H_2O	13	~170	543
C_3H_6	10	~180	344
SF_6	10	(~184)[c]	223
$(CH_3)_2CO$	9	~190	78
NH_3	15	~209	<6

[a] Proton affinity values taken from Table I in G. R. Freeman, *Radiation Res. Rev.*, **1**, 1 (1968). Extrapolation of the values for methanol and ethanol leads to the estimate $PA(C_3H_7OH) \approx 200$ kcal/mol. [b] 100-Torr alcohol, 350°, 3.1×10^{18} eV/g. [c] Estimated by interpolation, from a plot of *PA* against *G*(ether).

Although the addition of a small amount of propylene inhibited ether formation, the addition of a large amount sensitized the reaction (see the curve for *g*-(ether) in Figure 4). The sensitization must result mainly from reactions 8 and 9. The proton affinity of

$$C_3H_6 \rightsquigarrow C_3H_6^+ + e^- \qquad (8)$$

$$C_3H_6^+ + PrOH \longrightarrow C_3H_5 + PrOH_2^+ \qquad (9)$$

the allyl radical (174 kcal/mol, estimated from $D(C_3H_5\text{–}H) = 85$ kcal/mol[5] and $IP(C_3H_6) = 224$ kcal/mol[6]) is smaller than that of propanol (~200 kcal/mol, footnote *a*, Table III), so reaction 9 is exothermic. The *W* values of isopropyl alcohol and propylene, 24.2[7] and 24.8 eV,[8] respectively, are approximately equal to each other, so one would not expect to find an enhancement of *G*(ether) at high propylene concentrations; *G*(ether) is calculated on the basis of the total energy absorbed by the gas mixture. The slight enhancement of *G*-(ether) at high propylene concentrations shown in Figure 4 may be an indirect result of the propylene inhibition of the free-radical decomposition of the alcohol that occurs simultaneously in these systems.[9]

From the results in Table III one may speculate that the proton affinity of sulfur hexafluoride is approximately 184 kcal/mol.

Effect of Dose. The decrease in ether yield with increasing dose (Figure 3) was due to the accumulation of the radiolysis products acetone and propylene in the system. Acetone and propylene were produced by free-radical chain reactions,[9] and both inhibit ether formation (Table III). The water produced as a conjugate product to the ether would make only a small contribution to the observed dose effect, because water is a relatively inefficient inhibitor (Table III).

Effects of Pressure and Temperature. The slope of a log–log plot of the ether yield against the alcohol pressure equals $(n - 1)$, where n is the overall order of the ether formation mechanism. The order of ether formation was therefore zero at both 325 and 350° and at both 2.9×10^{17} and 3.2×10^{18} eV/g (Figure 2). If the values of the rate constants of reactions 4_m and 5_m, k_{4_m} and k_{5_m}, respectively, were independent of the value of m for $m > 2$, the order of ether formation by the mechanism $(1 - 6_m)$ would be ≥ 0.5.[4] The observed zero order might indicate that the values of one or both of k_{4_m} and k_{5_m} decrease with increasing m for $m \geq 2$. The average value of m in the system must increase with increasing alcohol pressure.

Inhibition of ether formation by the simultaneously produced acetone and propylene would also tend to reduce the order below 0.5.

It is somewhat surprising that the activation energy of ether formation is independent of alcohol pressure; $E_a = 40 \pm 1$ kcal/mol over the twentyfold pressure range studied (Figure 1). An analogous situation exists in ethanol vapor, where the activation energy of ether formation is 43 ± 4 kcal/mol, independent of alcohol pressure.[4] A detailed interpretation of these activation energies would require information about the effects of temperature and pressure on the distribution of m values in the systems (*cf.* reaction 3_m). Unfortunately, this information is not yet available.

The mean lifetimes of the ions with respect to neutralization under the present conditions were a few milliseconds, and the mean reaction chain lengths were a few tens, so the mean time required for a reaction cycle $(4_m + 5_m)$ was of the order of 10^{-4} sec. However, it is not yet possible to estimate the way in which this time is distributed amongst the various reactions 4_m and 5_m.[10]

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(6) R. W. Kiser, "Introduction to Mass Spectrometry and its Applications," Prentice Hall, Inc., Englewood Cliffs, N. J., 1965.

(7) P. Alder and H. K. Bothe, *Z. Naturforsch.*, **20a**, 1700 (1965).

(8) G. G. Meisels, *J. Chem. Phys.*, **41**, 51 (1964).

(9) H. J. van der Linde, unpublished results.

(10) NOTE ADDED IN PROOF. By analogy with the ethanol system[4] the equilibrium of major importance under the present conditions is probably (3_2), and reaction 4_2 might be better represented as

$$(PrOH)_2H^+ \longrightarrow Pr_2OH^+ + H_2O \qquad (4_2)$$

(4_2) is endothermic by 20–30 kcal/mol.

At methanol pressures in the vicinity of 0.1 Torr, Munson [M. S. B. Munson, *J. Amer. Chem. Soc.*, **87**, 5313 (1965)] observed reactions 10–12 in a mass spectrometer at 200°. The enthalpy of association in (10) is

$$MeOH_2^+ + MeOH \rightleftarrows (MeOH)_2H^{+*} \qquad (10)$$

$$\begin{tikzcd} & Me_2OH^+ + H_2O \qquad (11) \\ (MeOH)_2H^{+*} \arrow[ur] \arrow[dr, "MeOH"] & \\ & (MeOH)_2H^+ \qquad (12) \end{tikzcd}$$

probably slightly greater than that in the analogous water reaction [P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, *ibid.*, **89**, 6393 (1967)] or ~40 kcal/mol. This is equal to the thermal activation energy of the rate-controlling chain propagation reaction in the present 2-propanol system. Assuming unit collision efficiency for (12), $k_{11} \approx 10^6$ sec^{-1} for ions containing ~40 kcal/mol excitation energy. Such a low rate constant for ions that contain 40 kcal/mol excitation energy indicates that the rate controlling step in the thermal chain is (4_2), not (5_2).