13C-NMR Study of the Compounds Resulting from the Reaction of 5-Methylene-2-norbornene with Trifluoroacetic Acid

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ABSTRACT

Isomerization of the adduct resulting from the protonation of 5-methylene-2-norbornene by trifluoroacetic acid was studied by ^{13}C-NMR spectroscopy. Relative rate constants were determined under various experimental conditions. The influence of temperature, solvent, and relative reactant concentrations was examined.

Several terpenes are natural monomers which can be polymerized by cationic initiation. However, propagation is accompanied by many side reactions such as transfer and isomerization of the carbocation. Unfortunately, very few basic studies relative to these problems have been made. In this paper we study the kinetics of the isomerization of the cation resulting from the reaction of 5-methylene-2-norbornene with trifluoroacetic acid.

A study [1] of the compounds resulting from the reaction of 5-methylene-2-norbornene (M) with various protonic acids (A) confirmed that, as suggested by Kennedy and Makowski [2], isomerization of the initial carbocation takes place. In this study [1] the com-

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plete structures of the adducts IA and IIA relative to these carbo-
cations were determined.

IA   IIA
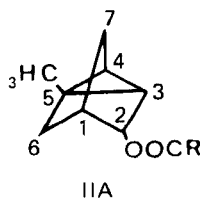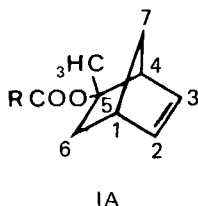
In addition, a preliminary examination of the influence of the nature
of A and of the initial ratio $(A)_0/(M)_0$ on the relative proportion of IIA
and IA was carried out.

The present article is devoted to a detailed study of the transforma-
tion of IA into IIA (IA-IIA) when A is trifluoroacetic acid. The follow-
ing points are examined:

Mechanism of the isomerization.
Values of the activation parameters.
Study of the ratio (IIA)/(IA) obtained at the end of protonation. For
a reaction carried out at stoichiometry ($(A)_0 = (M)_0$), the end of the

protonation corresponds to the moment when the peaks relative to the
monomer are no longer present in the NMR spectrum.

EXPERIMENTAL

A solution of trifluoroacetic acid $(A)_0 = 4$ mol/L, was added to a

3.6 mol/L solution of M. Solvents were CCl_4, $C_6H_5NO_2$, CH_2Cl_2, and

$CHCl_3$. $(A)_0/(M)_0$ is calculated from the weights of the reactants.

Five minutes after mixing the reactants (M is completely consumed),
the solvent is evaporated under vacuum.

All experimental data were obtained by ^{13}C-NMR analysis. A micro-
cell was used to separate the locking substance (D_2O). The same sam-
ple was used for kinetic studies.

Spectra were recorded by the gated decoupling technique to mini-
mize the NOE. (IIA)/(IA) is proportional to the ratio of the area of the
peaks attributed to the methylene carbon in the β-position of the methyl
group. We assume that the relaxation time is the same in both IIA and
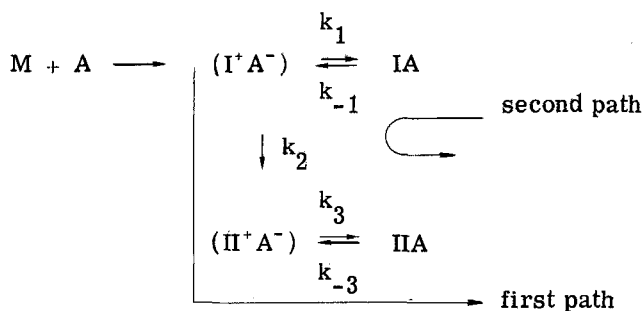IA.

RESULTS AND DISCUSSION

Analysis of the Different Steps of the Process

When an equimolar quantity of A is added to 5-methylene-2-norbornene, it is consumed rapidly and completely. After 5 minutes a mixture of IA (80 ± 5%) and IIA (20 ± 5%) is formed. (IIA)/(IA) increases with time, and IIA can be formed quantitatively. The time for the complete transformation of IA into IIA ranges from several hours to 2 weeks, depending on the temperature and the nature of the solvent.

We tried to induce the reverse reaction IIA→IA by adding trifluoroacetic acid to IIA but observed only the formation of a tar which did not contain IA.

We propose the following reactional scheme which takes into account the fact that isomerization IA→IIA is a complete and irreversible reaction:

$$
M + A \longrightarrow
\begin{array}{l}
(I^+A^-) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} IA \\[2ex]
\qquad\qquad\qquad \text{second path} \\[2ex]
\downarrow k_2 \\[2ex]
(II^+A^-) \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} IIA \\[1ex]
\qquad\qquad\qquad\qquad \text{first path}
\end{array}
$$

According to this scheme, two reaction paths lead to IIA. However, in both cases, the process begins by protonation of M which is rapid. During this step the concentrations of the ionic species are high because the acid AH solvates the counteranion A^- and the dielectric constant of the medium is high.

The first path consists of the direct isomerization of I^+A^- to II^+A^- followed by the formation of IIA. The second path involves the slow formation of the ion pair I^+A^- from IA followed by the isomerization of I^+A^- to II^+A^-.

The kinetics of these two paths are sufficiently different to be studied independently, at least as a first approach.

The protonation of M is too rapid to be studied by ^{13}C-NMR. On the other hand, the variations of (IIA)/(IA) with time can be followed by this technique, thus providing information on the isomerization of I^+.

Kinetic Study of the Isomerization IA-IIA by Second
Path Relative Kinetic Equations

These reactions are

$$-\frac{d(IA)}{dt} = k_1(IA) - k_{-1}(I^+A^-) \tag{1}$$

$$-\frac{d(I^+A^-)}{dt} = k_2(I^+A^-) + k_{-1}(I^+A^-) - k_1(IA) \tag{2}$$

$$-\frac{d(II^+A^-)}{dt} = k_{-3}(II^+A^-) - k_3(IIA) - k_2(I^+A^-) \tag{3}$$

$$-\frac{d(IIA)}{dt} = k_3(IIA) - k_{-3}(II^+A^-) \tag{4}$$

Using the assumption that a stationary state occurs:

$$-\frac{d(IA)}{dt} = k_1(IA) - k_{-1}(I^+A^-) \tag{1}$$

$$0 = k_2(I^+A^-) + k_{-1}(I^+A^-) - k_1(IA) \tag{2'}$$

$$-\frac{d(IA)}{dt} = \frac{k_1}{1 + \dfrac{k_{-1}}{k_2}}(IA) \tag{5}$$

The integrated form is

$$\ln\frac{(IA)_0}{(IA)} = \frac{k_1}{1 + \dfrac{k_{-1}}{k_2}}\, t, \quad \text{with } (IA)_0 = (IA) + (IIA)$$

$$\ln \left(1 + \frac{(IIA)}{(IA)} \right) = \frac{k_1}{1 + \frac{k_{-1}}{k_2}} \, t$$

We determined the rates of the reaction at 24, 47, 58, 62, and 76°C. The results are reported in Table 1 and Fig. 1.

Data reported in Fig. 1 show that the variations of $\ln \left[1 + \frac{(IIA)}{(IA)} \right]$ with respect to time at several temperatures are linear. This shows that the order of the kinetic step is 1 with a rate constant of

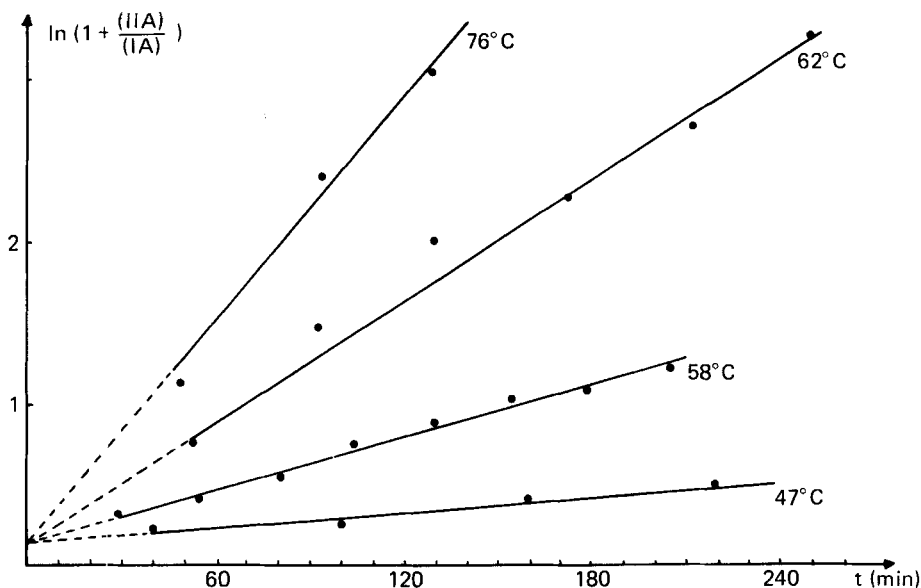$$k = \frac{k_1}{1 + \frac{k_{-1}}{k_2}}$$

FIG. 1. Variations of $\ln \left[1 + \frac{(IIA)}{(IA)} \right]$ with respect to time at different temperatures.

TABLE 1. Dependence of the Ratio $(IIA)/(IA)$ on the Temperature and Corresponding Value of $\ln\left[1 + \frac{(IIA)}{(IA)}\right]$; Reaction in the Bulk, $(A)_0 = (M)_0$

Temperature ($°C$)	Time (min)	$\dfrac{(IIA)}{(IA)}$ (^{13}C-NMR)	$\ln\left(1 + \dfrac{(IIA)}{(IA)}\right)$
24	20	0.23	0.20
	4,320	0.32	0.27
	10,080	0.59	0.46
47	40	0.25	0.22
	100	0.28	0.25
	160	0.43	0.36
	220	0.56	0.47
58	30	0.31	0.27
	55	0.48	0.4
	80	0.72	0.54
	105	1.03	0.71
	130	1.33	0.85
	155	1.77	1.01
	180	2.01	1.10
	205	2.4	1.21
62	50	1.12	0.75
	90	3.25	1.45
	130	6.9	2.1
	170	8.6	2.3
	210	13.3	2.7
	250	24.5	3.24
76	50	2.03	1.1
	90	13.3	2.6
	130	19.0	3.0

TABLE 2. Values of the Rate Constant $k = \dfrac{k_1}{1 + \dfrac{k_{-1}}{k_2}}$ Obtained at Different Temperatures

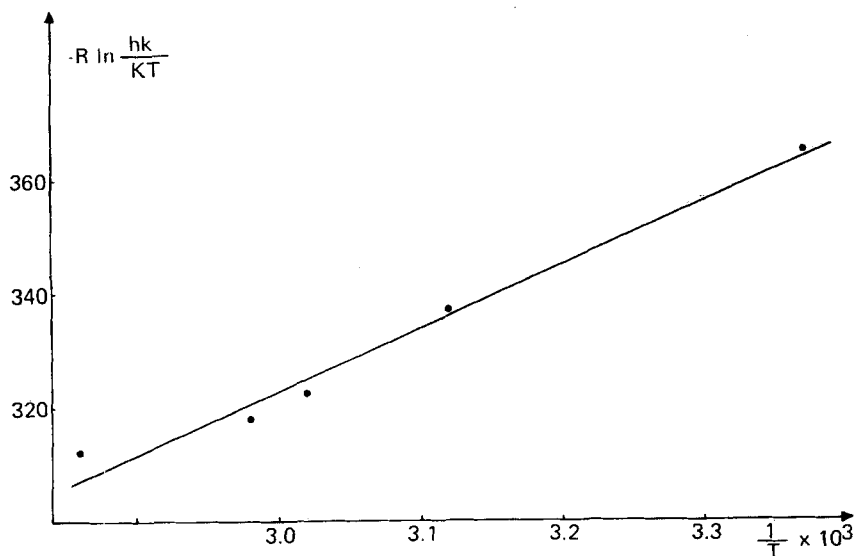| T (°C)	$k \ (s^{-1})$
24	5.0×10^{-7}
47	1.68×10^{-5}
58	9.2×10^{-5}
62	2.1×10^{-4}
76	3.67×10^{-4}

FIG. 2. Plot of $-R \ln (hk/KT)$ against $(1/T) \times 10^3$.

Values of k at different temperatures are reported in Table 2, and the Arrhenius plot is given in Fig. 2.
From the Arrhenius plot:

$\Delta H^* = 112$ kJ/mol

$\Delta S^* = 12.9$ J/K·mol

It is observed that the straight lines plotted in Fig. 1 converge to the same point. This corresponds to the ratio (IIA)/(IA) obtained at the end of protonation, i.e., M is completely consumed.

Study of the Dependence of (IIA)/(IA) on Various Experimental Parameters

The kinetics of the formation of IA and IIA from I^+A^- and II^+A^-, respectively, are very rapid. By assuming that the reverse reaction can be neglected, the preceding reaction scheme becomes

$$M + A \longrightarrow (I^+A^-) \xrightarrow{k_{-1}} IA$$

$$\downarrow k_2$$
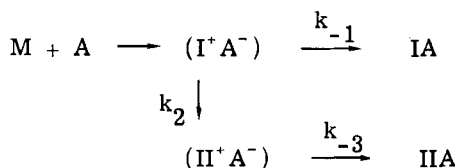
$$(II^+A^-) \xrightarrow{k_{-3}} IIA$$

with the corresponding kinetic equations

$$\frac{d(IA)}{dt} = k_{-1}(I^+A^-)$$

$$-\frac{d(II^+A^-)}{dt} = k_{-3}(II^+A^-) - k_2(I^+A^-)$$

$$\frac{d(IIA)}{dt} = k_{-3}(II^+A^-)$$

resulting in

$$-(II^+A^-) = (IIA) - \frac{k_2}{k_{-1}}(IA)$$

Now, the chemical shift of the peak attributed to the C_2 atom in IIA is the weight average of the shifts relative to the species (II^+A^-) and (IIA). Since its experimental value (85.4 ppm) is very close to that of carbon 1 in the following ester,
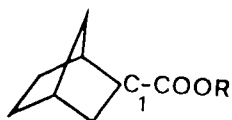
it is assumed that (II^+A^-) can be neglected as compared to (IIA).

TABLE 3. Dependence of the Ratio (IIA)/(IA) on the Amount of Trifluoroacetic Acid Added to a Solution of M in $CDCl_3$ at Room Temperature. $(M)_0 = 3$ mol/L. (IIA)/(IA) Was Determined 5 min after Acid Addition

$(A)_0/(M)_0$	(IIA)/(IA)	δC_5 IA (ppm)
0.35	0.14	94.3
0.52	0.16	94.4
0.92	0.23	94.6
1.26	1.17	95.2
1.73	∞	–

We did not find any reference relative to the chemical shift of a cation derived from a tricyclo(2,2,1,0)heptane; however, 2-norbornyl cation [4], whose shift is 125.3 ppm, can be considered as a satisfactory model and shows that if the contribution of II^+A^- is not negligible, the corresponding peak will appear at a much lower magnetic field than 85.4 ppm. Thus:

$$IIA/IA = k_2/k_{-1}$$

We studied the influence of several experimental parameters on this ratio. We report the results relative to the influence of $(A)_0/(M)_0$ in Table 3.

Table 3 shows that there is a sudden drastic increase in the ratio (IIA)/(IA) when $(A)_0/(M)_0$ is more than 1. Moreover, when the proportion of trifluoroacetic acid is increased, a shift of the peak corresponding to carbon C_5 of structure IA is observed. This means that the charge separation is increased. It is a well-known fact [5] that excess trifluoroacetic acid forms aggregates with the counteranion CF_3COO^-; this favors ion pair separation and consequently an increase of k_2 and a decrease of k_{-1}, which fits the increase of (IIA)/(IA) we observed.

The dependence of (IIA)/(IA) on temperature is reported in Table 4, which shows that, in the range of temperatures considered, (IIA)/(IA) does not vary, indicating that a changing in temperature varies k_2 and k_{-1} in the same proportion. This indicates that the Arrhenius parameters of these two reactions are probably very close.

The influence of the nature of the solvent is reported in Table 5. Examination of Table 5 shows that (IIA)/(IA) increases with an increasing dielectric constant of the medium. It is a well-known fact that in-

TABLE 4. Dependence of the Ratio (IIA)/(IA) on Temperature; Solvent CCl_4; $(A)_0 = (M)_0 = (A)_0 = (M)_0 = 1.7$ mol/L

t (°C)	(IIA)/(IA)
3	0.2
39	0.2

TABLE 5. Dependence of the Ratio (IIA)/(IA) on the Nature of the Solvent; $(M)_0 = 1.5$ mol/L, Room Temperature. (IIA)/(IA) was Determined 5 min after Acid Addition

$(A)_0/(M)_0$	Solvent	(IIA)/(IA)	Dielectric constant
0.86	$C_6H_5NO_2$ [a]	0.5	35
0.92	$CDCl_3$	0.23	4.8
0.99	CCl_4	0.2	2.2
0.93	C_6D_6	0.2	2.2
0.95	CH_2Cl_2 [a]	0.47	9.1

[a]When this solvent is used, a polymer with structure poly(IIA) (shown by ^{13}C-NMR) is formed. This minimizes the corresponding value of (IIA)/(IA).

creasing the dielectric constant of the solvent stabilizes the ionic form. When ϵ increases, k_{-1} decreases; if k_2 is constant, this fits our results. However, it is more probable that k_2 increases with increasing ϵ because an increase in the dielectric constant of the medium favors ion pair dissociation in the transition state.

The decrease of k_{-1} is corroborated by the fact that in nitrobenzene the peak relative to the carbon C_5 of IA is shifted toward low field (0.75 ppm).

Another experiment relative to the influence of the dielectric constant of the medium was carried out. When nitrobenzene is added to a reaction mixture containing 80% IA and 20% IIA at 24°C, k increases from 5×10^{-7} to 5.2×10^{-6} s^{-1}. Since increasing the polarity of the medium usually favors ionic species formation, it can be inferred that when the dielectric constant of the medium increases, k_1 increases

and k_{-1} decreases. Since k_2 increases, this set of observations is perfectly consistent.

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