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# CARBON-14 ISOTOPE EFFECTS IN THE FORMOLYSIS AND TRIFLUOROACETOLYSIS OF 2-ARYL-(ARYL-$^{14}$C)-ETHYL p-NITROBENZENESULFONATES

Yasuhide Yukawa, Takashi Ando, Mitsuru Kawada,
Katsuo Token, and Seung-Geon Kim
The Institute of Scientific and Industrial Research,
Osaka University, Suita, Osaka, Japan

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In a previous paper (1), we reported the results of the carbon-14 kinetic isotope effects in the acetolysis of 2-phenyl-(phenyl-1-$^{14}$C)-ethyl p-nitrobenzenesulfonate Ia, and 2-(4-methoxyphenyl-(phenyl-1-$^{14}$C))-ethyl p-nitrobenzenesulfonate IIa. It is concluded that the observed value ( $k^{12}/k^{14}$ =1.028) in the acetolysis of IIa indicated the existence of a change in the bond force constant of phenyl-1 carbon atom in the rate-determining step demonstrating the importance of the anisyl participation, while the value in Ia ( $k^{12}/k^{14}$ =1.002 ) showed that the phenyl participation was not be significant.

In this paper, we report the carbon-14 isotope effect of Ia and IIa in formic and trifluoroacetic acid. Ia and IIa were formolyzed at 60.00 and 30.00°C, by the sealed ampoule technique. In trifluoroacetic acid, Ia was solvolyzed at 45.00, also under the buffered condition with sodium trifluoroacetate at 30.00, and IIa at 0.0°C. After quenching the reaction mixtures by

I $C_6H_5CH_2CH_2X$ II $p\text{-}CH_3OC_6H_4CH_2CH_2X$
a : $X = O_3SC_6H_4NO_2\text{-}p$ b : $X = O_3SC_6H_4CH_3\text{-}p$

rapid cooling, and pouring onto ice-water, the sulfonates were precipitated quantitatively. The amount of reaction, specific activity of the purified esters, and the calculated carbon-14 isotope effect in formolysis and also those in trifluoroacetolysis are listed in Table I and II, respectively.

Table I

Carbon-14 Kinetic Isotope Effects in the Formolysis of 2-Aryl-(aryl-1-$^{14}$C)-ethyl p-Nitrobenzenesulfonates

| Reactant | Time, min | % Reaction | Specific Activity[a)] | $k^{12}/k^{14}$ |
|---|---|---|---|---|
| Ia[b)] | 0 | 0 | 2.068 | |
| | 125 | 39.8 | 2.088 | 1.020 |
| | 170 | 50.2 | 2.097 | 1.020 |
| | 225 | 60.3 | 2.115 | 1.025 |
| | 290 | 69.5 | 2.122 | 1.022 |
| | 390 | 78.9 | 2.140 | 1.023 |
| | | | mean value | 1.022 ± 0.002[d)] |
| IIa[c)] | 0 | 0 | 1.751 | |
| | 61 | 39.8 | 1.778 | 1.031 |
| | 126 | 59.3 | 1.787 | 1.023 |
| | 221 | 79.7 | 1.817 | 1.025 |
| | | | mean value | 1.026 ± 0.003[d)] |

a) mCi $mol^{-1}$. b) 60.00 ± 0.02°C, $c = 0.065\ mol\ l^{-1}$, $k_1 = 6.73 \times 10^{-5} sec^{-1}$.

c) 30.00 ± 0.02°C, $c = 0.059\ mol\ l^{-1}$, $k_1 = 1.20 \times 10^{-4} sec^{-1}$.

d) Probable error of the mean.

Table II

Carbon-14 Kinetic Isotope Effects in the Trifluoroacetolysis of 2-Aryl-(aryl-1-$^{14}$C)-ethyl p-Nitrobenzenesulfonates

| Reactant | Time, min | % Reaction | Specific Activity[a)] | $k^{12}/k^{14}$ |
|---|---|---|---|---|
| | 0 | 0 | 1.628 | |
| | 71 | 37.93 | 1.651 | 1.030 |

Table II (continued)

| | | | | |
|---|---|---|---|---|
| Ia$^{b)}$ | 130 | 60.29 | 1.665 | 1.025 |
| | 171 | 65.43 | 1.677 | 1.029 |
| | 225 | 73.20 | 1.693 | 1.031 |
| | | | mean value | 1.029 ± 0.002$^{e)}$ |
| Ia$^{c)}$ CF$_3$CO$_2$Na added | 0 | 0 | 1.628 | |
| | 130 | 41.37 | 1.663 | 1.033 |
| | 180 | 51.28 | 1.677 | 1.036 |
| | 320 | 69.52 | 1.696 | 1.032 |
| | | | mean value | 1.034 ± 0.002$^{e)}$ |
| IIa$^{d)}$ | 0 | 0 | 1.332 | |
| | 360 | 51.79 | 1.357 | 1.027 |
| | 480 | 61.49 | 1.386 | 1.045 |
| | | | mean value | 1.036 ± 0.009$^{e)}$ |

a) mCi mol$^{-1}$. b) 45.00 ± 0.02°C, c= 0.065 mol l$^{-1}$, k$_1$= 11.05 $\times$ 10$^{-5}$sec$^{-1}$.
c) 30.00 ± 0.02°C, [CF$_3$CO$_2$Na] = 0.1 mol l$^{-1}$, and c= 0.065 mol l$^{-1}$,
k$_1$= 5.96 $\times$ 10$^{-5}$sec$^{-1}$. d) 0.0± 0.1°C, c= 0.059 mol l$^{-1}$, k$_1$= 3.15$\times$10$^{-5}$sec$^{-1}$.
e) Probable error of the mean.

Both Ia and IIa showed a definite positive carbon-14 isotope effect in the formolysis and in the trifluoroacetolysis, though no isotope effect was found in the acetolysis of Ia. This observation indicates a change in the bonding of phenyl-1 carbon atom in the rate-determining step demonstrating the presence of phenyl participation as well as anisyl participation in the formolysis and in the trifluoroacetolysis.

Lee et al. (2) found Ib to undergo scrambling nearly to completion (45%) and IIb completely (50%) in formolysis, and Nordlander et al. (3) did complete scrambling (50%) in the trifluoroacetolysis of Ib. Furthermore, Snyder et al. (4) studied the stereochemistry in the solvolysis of threo-1,2-dideuteriophenylethyl p-bromobenzenesulfonate and observed that the retention of configuration amounted to 81% in formic acid and to 98% in trifluoroacetic acid, respectively.

Our observations not only agree with the results mentioned above, but also provide the most direct evidence of phenyl and anisyl participation in the formolysis and the trifluoroacetolysis of 2-arylethyl system.

## References

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