Polish J. Chem., **75**, 889–894 (2001) **COMMUNICATION**

Carbon-13 Isotope Effect for Carbon Dioxide Formation in the Reaction of Liquid Formic Acid with Uranium Trioxide

by M. Zieliński[1], A. Zielińska[1], N. Ogrinc[2], H. Papiernik-Zielińska[1] and I. Kobal[2]

[1] *Faculty of Chemistry, Jagiellonian University,*
Ingardena Str.3, 30-060 Cracow, Poland, Fax: (48-12) 634-05-15
[2] *J. Stefan Institute, SI-1000 Ljubljana, Jamova Str. 39, Slovenia*
Tel: + 386 61 1773 900 Fax No.: +386 61 177 38 11, 219

(Received November 10th, 2000; revised manuscript January 10th, 2001)

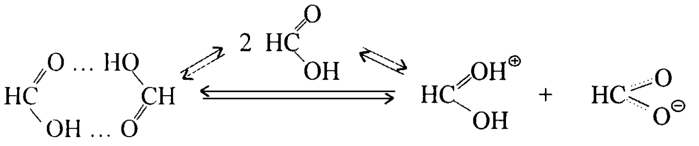
Continuing our investigations of the ^{13}C kinetic isotope effect for dehydration of liquid formic acid (FA) in the presence of different additives accelerating or inhibiting the decarbonylation of FA [1,2,3], we noticed that formic acid mixed under vacuum with uranium trioxide powder (provided by BDH-Chemicals-England) produces large quantities of carbon dioxide already at room temperature. The decarbonylation of FA proceeds with measurable rate in the presence of solvated UO_3 above 343 K only. Since this was unexpected result we examined the ^{13}C KIE for formation of both products of FA decomposition, CO_2 and CO, between 20–130°C. The isotopic results for decarbonylation of liquid FA in the presence of UO_3, UO_4 and $UO_2(HCOO)_2$ and for oxidation of HCOOH with fresh UO_4 have been submitted to Polish J. of Chemistry as fully understood at the chemical and isotope effect level. The delta PDB and the related carbon-13 kinetic isotope effects for carbon dioxide formed immediately after mixing 7.687 g of uranium trioxide (BDH England, poole 6588750) with 10 cm^3 of liquid FA (Merck) under vacuum are presented in Table 1. The evolution of CO_2 practically ceased at 23°C after 21 h and only traces of CO_2 have been extracted from r.v. during the subsequent 40 h at 298 K. The slow but measurable production of carbon dioxide has been observed between 343–393 K (exp. U2-U9). The violent production of carbon dioxide at room temperature (after 5 minutes of induction period) followed by "gentle boiling" has been observed also in the two supplementary series of reactions of 4.715 g of UO_3 with 10 cm^3 of HCOOH, carried out in vacuum reaction vessel at 18°C (291 K) and then, in the reaction of 8.374 g of UO_3 with 10 cm^3 of HCOOH/at 30.3°C (303.5 K). The amount of carbon dioxide produced at room temperature was proportional to UO_3 used in oxidation experiments (U-1: 0.9308 mmoles of CO_2/7.686 g UO_3 = 0.1211 at 23°C/21 h reaction time). No production of CO_2 was observed in the decomposition of liquid FA in the presence of fresh uranyl formate obtained in the reaction of UO_3 with liquid formic acid.

The room temperature oxidations of formic acid with solid uranium trioxide powder were accompanied by large ^{13}C isotope fractionation. ^{13}C KIE = 1.0487 for 0.445 mmoles of CO_2 obtained during 4 h oxidation of 10 cm^3 of FA at 291 K (R_{so}/R_{pf} = 1.0487, δ (PDB) = −68.23 ± 0.08). The subsequent portions of CO_2 were produced in the higher 343.16–384.16 K temperature interval with ^{13}C KIE located in the range 1.028–1.031. Fractionation of carbon-13 in the course of oxidation of FA with UO_3 is much higher than ^{13}C KIE's, observed in the oxidation of liquid FA with freshly prepared uranium peroxide (located in the range 1.016–1.027 in the temperature interval 294–393 K). Interpretation of the ^{13}C KIE data concerning the oxidation of FA with commercial uranium trioxide is a less straightforward task than interpretation of ^{13}C KIE's in the oxidation of FA with UO_4 or decarbonylation of this acid in the presence of UO_3 or UO_4. The fast initial oxidation of FA with UO_3 BDH England provides carbon dioxide characterized by (R_{so}/R_{pf}) = 1.0478_3; a value found in decarbonylation reactions, which involve ^{13}C–^{16}O bond rupture in the rate determining step. This is an uncommon phenomenon in oxidation reactions, where the carbon–hydrogen bonds are usually exposed to the attack by the oxidizer and where large deuterium and tritium KIE's are observed. Two possible reasons might be suggested as responsible for this large ^{13}C KIE: The uranium trioxide powder, produced by BDH Chemicals England, is contaminated slightly with highly reactive fluorine derivatives, which attacking FA substitute for the hydroxyl oxygen in the process require rupture of the carbon–oxygen bond in the rate determining step. The second phenomenon leading to the rupture of the carbon–oxygen bond of FA might be related with induced by alpha radiolysis impairments in the solid UO_3 reacting with penetrating the solid formic acid molecules. The number of reactive defects is proportional to the solid trioxide, used in the oxidative reaction. The new scientific example, 23/U-1, presented in Table 1, is a challenge for isotope chemists [4].

The ^{13}C KIEs in the oxidation of formic acid with uranium trioxide are higher than the ^{13}C KIEs in the oxidation of formic acid with uranium peroxide, especially in the case of initial room temperature oxidation of HCOOH with commercial UO_3. Assuming that the uranium trioxide is a pure compound with a solid structure modified by alpha radiation defects only, two explanations of the experimental data presented in Table 1 can be given. Carbon dioxide is produced in a two-step reaction with the first step involving the rupture of the ^{13}C–^{16}O bond (as in decarbonylation reaction) accompanied with large ^{13}C KIE. The "reactive uranium peroxide" [4] imbedded in the structure of the solid UO_3 has been suggested by us, but the freshly prepared UO_4 (used as the oxidant of liquid formic acid) does not show this ^{13}C isotope effect anomaly. The second pathway invoked to rationalize the fast initial oxidation of liquid FA is the oxidation of FA with alpha radiation defects consisting of "UO_2^{2+} vacancies" and of located nearby oxidizing species like O_2^{2-} or O_3^{2-}, *etc*. Formate anions, $HCOO^-$, react with vacancies and the properly oriented and immobilized (in the solid UO_3) species are oxidized subsequently with labile and reactive negatively charged di- or three-atom-oxygen species, as shown explicitly in equations (1,1a–e, 2a–b) and (3).

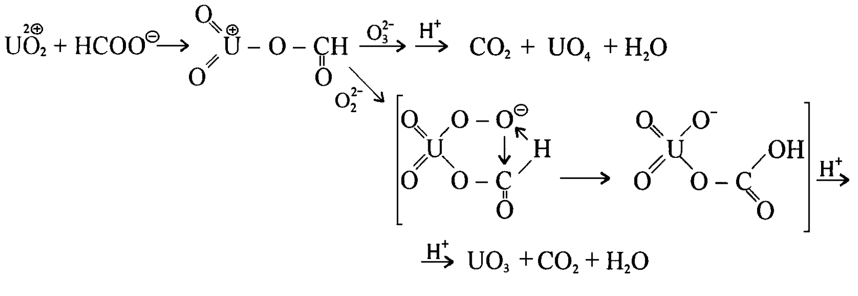
Table 1. Isotopic composition of carbon dioxide produced in the reaction of 265.110 mmoles of HCOOH, 10 cm^3 with 7.686 g of uranium trioxide, UO_3, distributed by BDH Chemicals, England (poole 6588750).

Reaction temp.°C and sample no.	mmoles of CO_2 produced	Fraction "f" of oxidation of FA	δ (PDB) for carbon dioxide isolated	R ($^{13}C/^{12}C$) carbon isotope ratio	(k_{12}/k_{13}) experi-mental
23/U-1	0.9308	0.00351	−67.46 (pf)	0.0104791 (pf) 0.0109803 (so)	1.0479
70.15/U-2	0.01117	0.0000423	−52.49 (pf)	0.0106474 (pf) 0.0109821 (so)	1.0314
92.2/U-3	0.0569	0.000215	−53.49 (pf)	0.0106361 (pf) 0.0109821(so)	1.0325
93.3/U-4	0.1076	0.000408	−48.71 (pf)	0.0106898 (pf) 0.0109822 (so)	1.0276
101.1/U-5	0.1428	0.000542	−49.63 (pf)	0.0106795 (pf) 0.0109828 (so)	1.0284
101.15/U-6	0.0946	0.000359	−50.82 (pf)	0.0106661 (pf) 0.0109835 (so)	1.0298
111.0/U-7	0.0990	0.000377	−51.79 (pf)	0.0106552 (pf) 0.0109849 (so)	1.0309
17.5/U-8	0.0090	0.0000344	−50.01 (pf)	0.0106752 (pf) 0.0109872 (so)	1.0292
121.8/U-9	0.0180	0.0000690	−56.21 (pf)	0.0106056 (pf) 0.0109872 (so)	1.0360



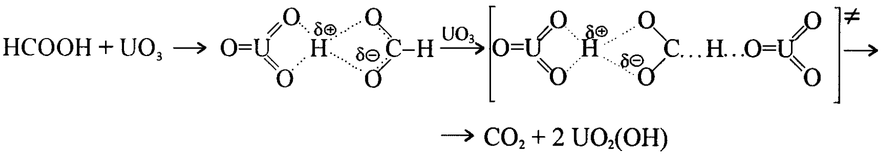
(0)

$$UO_3 \xrightarrow{\alpha\ \text{radiation},\ O_2} UO_2^{2+}\ \text{vacancy} + O_3^{2-} \quad (1)$$

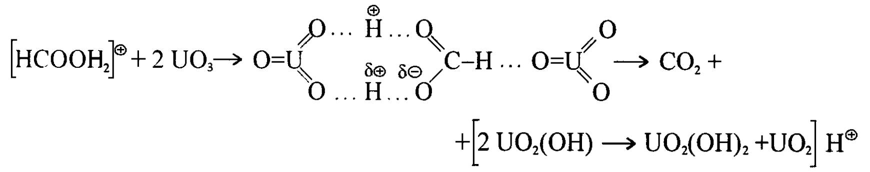


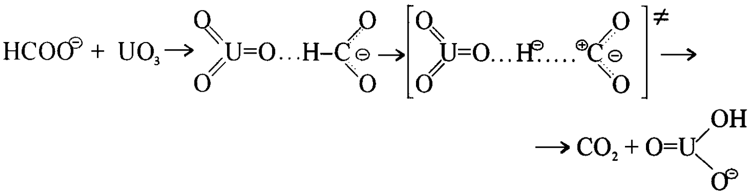
(1a)

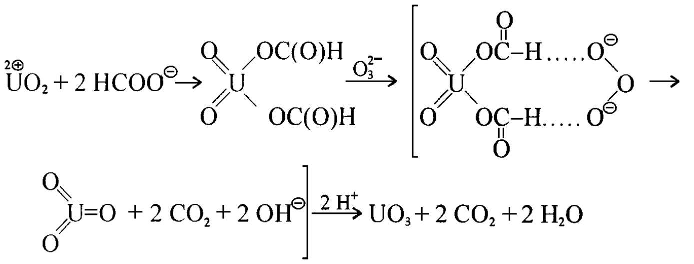
(1b)

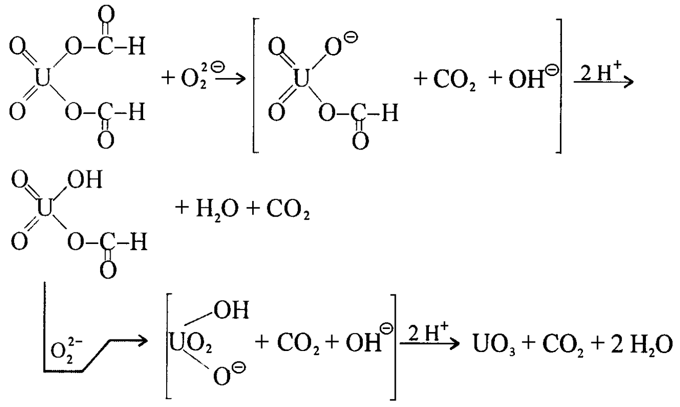


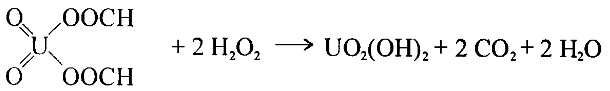
(1c)


(1d)

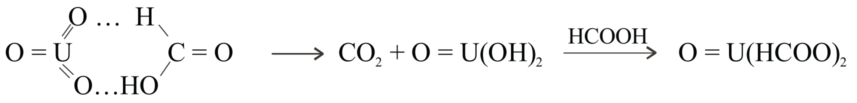

(1e)

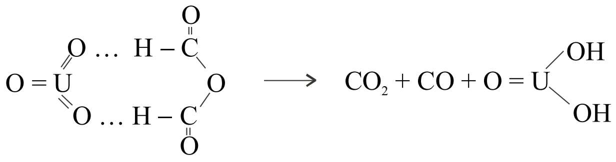

(2a)


(2b)


(3)

The oxidation of FA, "catalyzed" by alpha radiation of uranium, can explain the large ^{13}C oxidation KIEs only if the oxidized $HCOO^-$ anions had been depleted in ^{13}C with respect to "bulk" formic acid in the dimmer/monomer equilibria, in the preferable formation of anions $HCOO^-$ containing light ^{12}C and in the diffusion of $HCOO^-$ to the vacancy. The final combination of UO_2^{2+} center with $HCOO^-$ is a probably fast and irreversible process proceeding without $^{13}C/^{12}C$ fractionation/discrimination. After reaction of $HCOO^-$ with all accessible radiation defects (that is after "saturation" of all reactive centers) the subsequent slow oxidation proceeds with smaller ^{13}C KIE than in the case of initial fast room temperature oxidation of formic acid, but still larger one than in the oxidation of FA with uranium peroxide, fresh one UO_4. It is highly probable that the larger ^{13}C KIE, observed in the slow oxidation of FA with UO_3 than in the oxidation of FA with UO_4, is a consequence of hydrogen being at large distance from carbon of formate in the TS in the course of its motion to the oxygen of UO_3, what causes the lack of the compensation of C–H bending vibrations contributions of $H\text{-}^{13}COO^-$ to ^{13}C KIE. But at present state of the isotope effect studies one cannot reject the possibility that the large ^{13}C fractionation, observed in the room temperature oxidation of formic acid with old uranium trioxide, UO_3, produced by BDH England, may be interpreted also as the result of two equilibrium fractionations augmenting the third kinetic one, related with ^{13}C–H bond rupture. The monomer HCOOH and anion $HCOO^-$ are depleted in ^{13}C. The ionic character of the $HCOO^-$ bonding in uranyl formate should not contribute greatly to ^{13}C fractionation, but covalent bonding should. The $^{13}C–^{1}H$ bond rupture in the final oxidation kinetic step is accompanied by the usual ^{13}C KIE or is assisted by tunneling. Diffusion of monomeric $HCOO^-$ species to the inner "radiation defects" might also contribute to the observed ^{13}C fractionation. Carbon dioxide formation might be preceded by intermediate carbonates as shown in equation (1b). ^{13}C KIE's in the subsequent slow oxidations of FA with UO_3 (experiments U2–U9) are located in the 1.028–1.033. The last results can be reproduced by calculation scheme, which involves besides C–H stretching vibration the deformation modes of motion assisting the transfer of two hydrogen atoms to U(VI) in the course of its reduction to U(IV). Formic anhydride might appear also to be better reducing agent than FA itself.

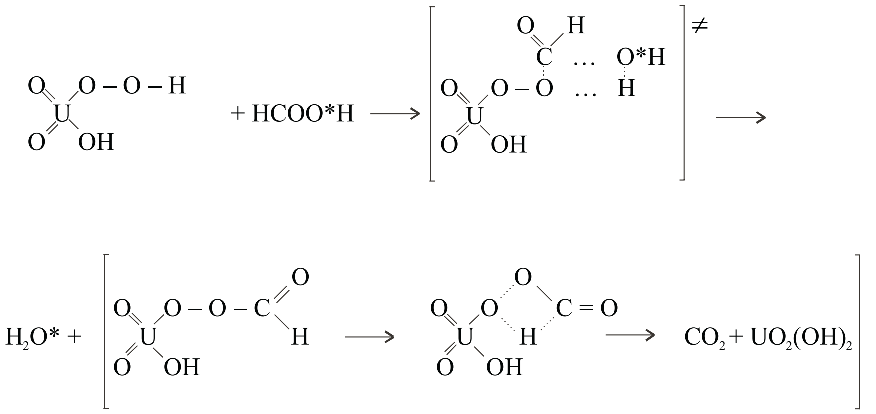




The main reaction between uranium trioxide and liquid formic acid provides directly uranyl formate at higher reaction temperature (373–400 K).

$$UO_3 + 2\,HCOOH \rightarrow UO_2(HCOO)_2 + H_2O$$

Alternative oxidation path of liquid formic acid with UO_3 containing traces of highly reactive forms of uranium peroxide within its solid structure is given below:



Acknowledgments

This study has been supported by the Polish State Committee for Scientific Research Grant No C-44/99, by the Ministry of Science and Technology of the Republic of Slovenia, by the J. Stefan Institute of Ljubljana, and partly by the Faculty of Chemistry of Jagiellonian University.

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