*cis*- and *trans*-conformers with an equal rotation of the rings, as for the neutral molecule, is retained for the cation in solution. The experimental value ($_mC$ = $38 \cdot 10^{-15}$ emu) is in accord with the angle of 48°.

Thus, the transition of 6,6′-biquinolyl from the neutral form to its diprotonated form does not noticeably affect the conformation of the molecule.

## References

1. S. G. Vul'fson, V. F. Nikolaev, and A. N. Vereshchagin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 2296 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1983, **32**, 2073 (Engl. Transl.)].
2. A. P. Timosheva, I. A. Kushnikovskii, S. G. Vul'fson, and A. N. Vereshchagin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 2771 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 2415 (Engl. Transl.)].
3. A. P. Timosheva, I. A. Kushnikovskii, S. G. Vul'fson, and A. N. Vereshchagin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 2761 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 2405 (Engl. Transl.)].
4. A. N. Vereshchagin and L. A. Grozina, *Teor. i eksp. khimiya* [*Theor. and Exp. Chem.*], 1968, 361 (in Russian).
5. K. Folting and L. Merrit, *Acta Crystallogr.*, 1977, **33**, 3275.
6. M. Lenner and O.Lindgren, *Acta Crystallogr.*, 1976, **32**, 1903.
7. P. Wormell and L. D. Ritchie, *J. Mol. Struct.*, 1990, **240**, 331.
8. R. J. W. Le Fevre, A. Sundaram, and K. M. S. Sundaram, *J. Chem. Soc.*, 1963, 3180.
9. R. J. W. Le Fevra and D. S. N. Murthy, *Austral. J. Chem.*, 1966, **19**, 1321.
10. S. G. Vul'fson, I. A. Kushnikovskii, A. P. Timosheva, and A. N. Vereshchagin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 615 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 534 (Engl. Transl.)].
11. A. L. McClellan, *Tables of Experimental Dipole Moments*, Rahara Enterprises, 8636 Don Carol Dr. El Cerrito, CA 94530,1989, **3**, 487.
12. A. N. Vereshchagin and S. G. Vul'fson, in *Konformatsionnyi analiz elementoorganicheskikh soedinenii* [*Conformational Analysis of Organoelement Compounds*], Ed. A. N. Pudovik, Nauka, Moscow, 1983 (in Russian).

*Received May 14, 1993*

---

# The experimental detection of a retro-Prince reaction exemplified by a homogeneous acid-catalyzed decomposition of isopentenols

***R. S. Ryabova* and G. F. Osipova***

*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,*
*4 ul. Kosygina, 117977 Moscow, Russian Federation.*
*Fax: +7 (095) 938 2156*

The occurrence of the retro-Prince reaction in the transformations of an equilibrium mixture of 2-methyl-3-buten-2-ol and 3-methyl-2-buten-1-ol in 24.9—49 % aqueous sulfuric acid at 25 °C has been experimentally proved.

**Key words**: acid catalysis; equilibrium mixture; isopentenols; Prince reaction.

Kinetic studies of the transformation of 2-methyl-3-buten-2-ol (**1**), 3-methyl-2-buten-1-ol (**2**), and 3-methyl-3-buten-1-ol (**3**)[1—3] in acidic media have shown that several consecutive reactions are involved and an equilibrium is established under the conditions studied.[3]

Previously[3] on the basis of kinetic and GLC data, a scheme was suggested for the transformations of an equilibrium mixture of alcohols **1** and **2** and isoprene (IP) in aqueous solutions of sulfuric acid (from 24.9 % to 49.76 %) at 25 °C.

The major reaction product under these conditions is 3-methylbutane-1,3-diol (**4**).

The reaction rates depend on the concentration of the catalyst ($H_2SO_4$). For example, in 25 % $H_2SO_4$ at 25 °C, the effective rate constants are 2.8 $min^{-1}$ for isomerization of **1** into **2**, $9.5 \cdot 10^{-2}$ $min^{-1}$ for dehydration of the **1** $\rightleftarrows$ **2** equilibrium mixture into IP, and $6.3 \cdot 10^{-2}$ $min^{-1}$ for hydration of **3** into 4.

However, when compound **1** was the starting material, a material unbalance[3] was revealed: $C_0{}^1 = C^1 + C^2 + C^3 + C^4 + C^{IP} + C^X$, where $C_0{}^1$ is the initial

---

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 2, pp. 332—334, February, 1994.

concentration of compound **1**, $C^1...C^4$ are the current concentrations of the products, and $C^X$ is the concentration of an unidentified product (~10 % based on the starting **1**).

In the present work we attempted to identify this product.

## Experimental

The experiments were carried out in a closed temperature-controlled glass vessel with an outlet for withdrawal of samples. Compound **1** was the starting material; its concentration did not exceed 0.2 *M*. Aliquots of the reaction mixture (5 mL) were cooled and neutralized with a 15 % solution of NaOH to pH 7. One half of the sample was mixed with chloroform. The products from both the aqueous and the organic layer were analyzed by GLC on a LKhM/U instrument with a flame ionization detector, and a 2m×4 mm stainless-steel column with 10 % Carbowax 20 M on 0.2—0.36 mm Inerton; argon at a flow rate of 40 mL $min^{-1}$ was used as the carrier gas. The temperature of the column was 80 °C.

The kinetics of the hydration of isobutylene in aqueous solutions of $H_2SO_4$ was studied by spectrophotometry (decrease in the optical density at 207 nm).

## Results and Discussion

In the aqueous part of the aliquot of the reaction mixture containing alcohol **1**, all three of the isomeric unsaturated alcohols and diol **4** were found. The organic phase contained alcohols **1**—**3**, IP, and *tert*-butyl alcohol (**5**). The formation of compound **5** under rather mild reaction conditions (25 °C) was unexpected. It should be noted that analysis of the products has shown that the concentration of **5** passed through a maximum as the concentration of **1** decreased with time. Analysis of the original alcohol **1** showed that it did not contain compound **5**.

The presence of alcohol **5** in the products of the transformation of unsaturated alcohol **1** in aqueous $H_2SO_4$ indicates that consecutive steps of the process involve the formation of isobutylene.

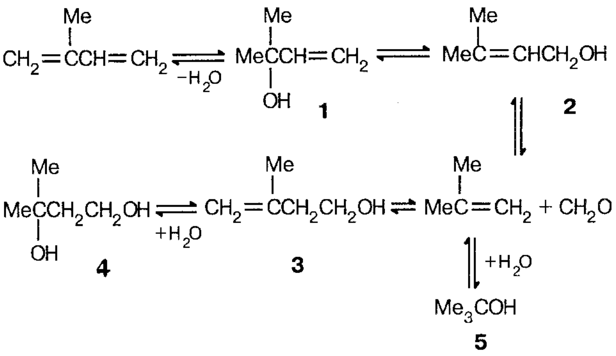
We estimated the rate constants of the hydration of isobutylene in aqueous sulfuric acid at 25 °C by spectrophotometry. They are rather great and amount to 0.8 $min^{-1}$ in 20 % $H_2SO_4$ and 2.0 $min^{-1}$ in 30 % $H_2SO_4$. Thus, the isobutylene formed during the transformations of isopentenols in aqueous solutions of $H_2SO_4$ is quickly hydrated to give compound **5**.

Thus, we suggested that through the action of acid catalysts isopentenols are cleaved to afford isobutylene and formaldehyde. Using a precise method for the microanalysis of formaldehyde,[4] we found ~$10^{-6}$ *M* of $CH_2O$ in the reaction media. Such a low concentration of $CH_2O$ may be due to its rapid reaction with unsaturated alcohols to yield hemiformals, as has been shown previously.[5]

In the reaction mixture (25 °C) that was stored for a long period (4 days), 4,4-dimethyl-5-hydroxymethyl-1,3-dioxane (DX) was detected (see Ref. 5). According to the data reported in Ref. 6, DX is the product of the condensation of alcohol **2** with $CH_2O$ under these conditions. The presence of DX is additional evidence for the formation of $CH_2O$ in the reaction medium.

Based on the established fact that isobutylene (or compound **5**) and $CH_2O$ are formed in the transformations of the equilibrium mixture of **1** and **2** in aqueous $H_2SO_4$, we present one of the possible schemes that account for the formation of the intermediate and final products (Scheme 1).

**Scheme 1**



As can be seen from this scheme, unsaturated alcohol **2** is the source of isobutylene and $CH_2O$, *i.e.*, decomposition of **2** in acidic media is the retro-Prince reaction.

It is quite probable that isobutylene formed in acidic media adds $CH_2O$ (the Prince reaction) to yield isomer **3** of isopentenols.

It is known[6] that condensation of isobutylene with formaldehyde in the presence of $H_2SO_4$ affords all three of the alcohols **1**—**3** and the products of their condensation with $CH_2O$ along with the major product, 4,4-dimethyl-1,3-dioxane.

Some researchers[7—9] believe that the interaction of isobutylene with $CH_2O$ gives alcohol **3** as the main product.

In our opinion, the presence of numerous condensation products in the reaction of acyclic olefins[6] and cycloolefins[10] with formaldehyde was due to the fact that the reactions were carried out at high concentrations of $CH_2O$ in acidic media, where its polymer hydrates of various compositions,[11] which can also participate in the reaction, are formed.

Under the conditions used in the present work, when the initial concentration of alcohol **1** did not exceed 0.2 *M*, the concentration of $CH_2O$ produced upon decomposition of isopentenols should be even lower. According to the reported data,[11] formaldehyde exists in dilute solutions in the $H_2O—H_2SO_4$ system as methylene glycol, and it is quite likely that its protonated form is reactive in the condensation with isobutylene yielding unsaturated alcohols **3** and **2**.

The work was carried out with the financial support of the Russian Foundation for Basic Research (Grant No. 93-03-18356).

## References

1. R. S. Ryabova, G. F. Oleinik, L. D. Abramovich, A. P. Troitskii, and M. I. Vinnik, *Zh. Org. Khim.*, 1976, **12**, 499 [*J. Ogr. Chem.*, 1976, **12** (Engl. Transl.)].
2. R. S. Ryabova, G. F. Osipova, and M. I. Vinnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 1016 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 886 (Engl. Transl.)].
3. R. S. Ryabova, G. F. Osipova, and M. I. Vinnik, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 1311 [*Bull. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 1021 (Engl. Transl.)].
4. T. Nash, *J. Biol. Chem.*, 1953, **55**, 416.
5. V. M. Zakoshanskii, Ph. D. (Chem.) Thesis, VNIINeftekhim, Leningrad, 1976 (in Russian).
6. S. K. Ogorodnikov and G. S. Idlis, *Proizvodstvo izoprena* [*Production of Isoprene*], Khimiya, Moscow, 1973 (in Russian).
7. J. W. Baker, *J. Chem. Soc.*, 1944, 296.
8. M. Hellin, M. Davidson, and F. Coussemant, *Bull. Soc. Chim. Fr.*, 1966, 1859.
9. V. I. Isagulyants, T. G. Khaimov, and V. R. Mel'nikov, *Usp. Khim.*, 1968, **37**, 61 [*Russ. Chem. Revs.*, 1968, **37** (Engl. Transl.)].
10. N. G. Volynskii, *Tsikloolefiny v reaktsii Prinsa* [*Cycloolefins in the Prince Reaction*], Nauka, Moscow, 1975 (in Russian).
11. R. S. Ryabova, A. U. Stepanyants, and G. F. Osipova, USSR Pat. № 1828647, 1990.

*Received May 31, 1993;*
*in revised form July 11, 1993*

---

# Leveling of reactivity for intramolecular radical substitution reactions in viscous media

***R. R. Rakhimov,[a]* A. I. Prokof'ev,[b] and Ya. S. Lebedev[a]***

[a] *N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,*
*4 ul. Kosygina, 117977 Moscow, Russian Federation.*
*Fax: +7 (095) 938 2156*
[b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
*28 ul. Vavilova, 117813 Moscow, Russian Federation.*
*Fax: +7 (095) 135 5085*

A leveling of the reactivity was found for intramolecular radical reactions in substituted 2-oxyphenoxyls in viscous media. A comparison of rate constants in toluene, hexane, pentane, and vaseline oil shows that fast reactions are decelerated more rapidly than slow reactions.

**Key words**: reactivity, radicals, viscosity.

The effect of molecular mobility on chemical reactivity[1] and the leveling of chemical reactivity in comparison with the liquid phase[2] have been found for bimolecular radical substitution in polymers. In a qualitative sence, the leveling manifests itself in the fact that fast reactions are decelerated much more rapidly on going to the solid phase than slow reactions. The following empirical relationship is obeyed:

$$k_s \sim k_f^m, \qquad (1)$$

where $k_s$ and $k_f$ are rate constants of the reactions in the solid and in the liquid phase, respectively, and $m = 0.5 \div 1$ (see Ref. 2). In the present work, similar regularities for monomolecular reactions are reported for the first time.

It was previously shown[3] that intramolecular radical substitution in substituted 2-oxyphenoxyls is decelerated in viscous media, and the time of chemical exchange, $\tau_{ex} = 1/k$ ($k$ is the monomolecular rate constant), is proportional to the time of rotational correlation of the radicals, $\tau_c$. The data available can be semiquanitatively interpreted in the framework of the model of the indi-

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 334—336, February, 1994.