THE EPR INVESTIGATION OF PHENYL-SUSTITUTED CARBON ACIDS FAST PROTON EXCHANGE REACTIONS

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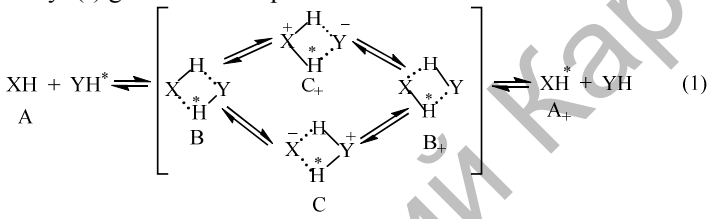
The EPR investigations of several substituted carbon acids proton exchange fast reactions (1) with semiquinone spin probe 3,6-di-tert.butyl-2-oxyphenoxyl (I) gives the next presented on table kinetic data.



Acid	k_{ex} (293K), l/мol·c	E_a, kJ/mol	pK_a
formic	$(4,5 \pm 0,2)\cdot 10^7$	7,1 ± 0,3	3,75
acetic	$(5,1 \pm 0,7)\cdot 10^7$	13,4 ± 0,4	4,75
benzoic	$(1,7 \pm 0,1)\cdot 10^8$	5,8 ± 0,2	4,17
phenylacetic	$(6,4 \pm 0,2)\cdot 10^7$	11,7 ± 0,7	4,28
2-quinolinic	$(1,4 \pm 0,4)\cdot 10^7$	9.0 ± 0,8	4,95
abietic	$(2,2 \pm 0,1)\cdot 10^8$	7,7 ± 0,3	-
cinnamic	$(2,5 \pm 0,1)\cdot 10^8$	5,8 ± 0,4	4,44
phenol	$(1,0 \pm 0,5)\cdot 10^6$	13,1 ± 0,9	-

The rates constant for phenol was obtained in medium of melted pure compound. The semiquinone radical I is paramagnetic H-acid, but doesn't exchange proton with alco-hols and water molecules. Presented table shows that benzoic acid has more protolytic activity i.e. the value of intermolecular proton exchange rate constant k_{ex} then formic and acetic acids, but separation of phenyl group from carboxylic group make protoly-tic activity of phenylacetic acid similar formic and acetic acids activity. Summary electronic conjugationon of benzene, ethylene and carboxylic group in cinnamic acid gives us the rate constant increasing. If the influence of big substituent in abietic acid has the difficult explanation, quinolynic group of 2-quinolynic acid tend to formation of zwitter-ion.

Репозиторий КарГУ