CLXXXIV.—*The Conductivities of Sodium and Potassium Derivatives of β-Ketonic Compounds in Alcoholic Solution.*

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THE molecular conductivities of the sodium and potassium derivatives of ethyl acetoacetate, acetylacetone, benzoylacetone, ethyl *iso*butyl- and *iso*amyl-acetoacetate, and also of sodium and potassium ethoxides and potassium iodide were determined in alcoholic solution at 25° at dilutions of 4 to 1024 litres. The values obtained for greater dilutions show considerable deviations due to the comparatively large errors unavoidable in such dilute solutions.

The measurements were carried out by the usual method with an induction coil and telephone. The alcohol was purified by refluxing with freshly burnt quicklime for 2—3 days, and after distillation had a specific conductivity of $0{\cdot}15 \times 10^{-6}$ mho.

The solutions of the sodium and potassium β-ketonic derivatives were prepared by the addition of the exact amount of alcoholic solution of the corresponding ethoxide of known strength to

slightly more than the theoretical quantity of the ketonic substance also dissolved in alcohol, the solution then being diluted with alcohol to the required volume. Dilution of the solutions during a series of conductivity measurements was effected by pipettes.

Ethyl acetoacetate was purified by washing, drying, and redistillation; b. p. 181°. Ethyl *iso*butylacetoacetate, b. p. 218°, and *iso*amylacetoacetate, b. p. 228°, were prepared by the method of Conrade and Limpach (*Annalen*, 1882, **214**, 137). (The sodio*iso*amyl derivative was found to be optically inactive.) Benzoylacetone after recrystallisation had m. p. 60°. Acetylacetone after drying and redistilling boiled at 137°.

The following tables give the molecular conductivity corresponding to dilution v, the values for ethyl sodioacetoacetate in parentheses being those obtained when the solvent contained 5·5% of water.

	$CH_3{\cdot}CO{\cdot}CHM{\cdot}CO{\cdot}CH_3$,		$C_6H_5{\cdot}CO{\cdot}CHM{\cdot}CO{\cdot}CH_3$,		$CH_3{\cdot}CO{\cdot}CMBu^s{\cdot}CO_2Et$,		
v.	M = Na.	M = K.	M = Na.	M = K.	M = Na.	M = K.	KI.
8	5·794	12·096	5·066	10·863	—	—	—
16	8·254	15·43	7·261	13·968	13·293	16·688	24·64
32	11·187	18·89	9·822	17·22	17·155	20·495	27·904
64	14·426	22·234	12·736	20·493	21·427	24·22	32·14
128	18·116	25·68	16·128	24·00	25·754	27·891	35·955
256	21·82	28·672	19·712	26·70	29·939	30·925	39·54
512	25·636	31·565	23·59	29·804	33·485	33·23	42·55
1024	29·927	33·95	27·34	32·307	36·864	35·84	45·261
2048	—	—	—	—	—	—	47·104
4096	—	—	—	—	—	—	47·514

	$CH_3{\cdot}CO{\cdot}CM(C_5H_{11}){\cdot}CO_2Et$,				$CH_3{\cdot}CO{\cdot}CMH{\cdot}CO_2Et$,	
	M = Na.	M = K.	NaOH.	NaOEt.	M = Na.	M = K.
4	—	—	—	—	3·103 (—)	7·0807
8	—	—	—	—	4·712 (7·567)	9·190
16	13·24	16·341	—	—	6·691 (10·688)	12·181
32	17·14	19·85	22·83	20·97	8·96 (14·080)	15·41
64	21·04	23·741	26·40	24·56	12·288 (17·536)	19·09
128	24·038	27·674	30·59	28·15	15·81 (21·376)	23·071
256	27·75	31·232	33·31	31·49	19·71 (25·446)	26·598
512	30·72	34·570	35·43	34·25	24·34 (29·747)	30·37
1024	32·932	36·966	37·89	36·66	28·74 (35·533)	33·38

The experiments show that these substances are conductors of electricity in ethyl-alcoholic solution, the molecular conductivity being only slightly less than that of potassium iodide.

Values for the limiting molecular conductivity at infinite dilution, as found by extrapolation of the curves obtained by plotting the logarithm of the molecular conductivity against the cube root of the concentration (which showed only slight curvature for low concentrations), were seen, when compared amongst themselves, to be inconsistent with the law of independent migration. Thus complete dissociation is not approached at the maximum dilution used (compare Robertson and Acree, *J. Physical Chem.*, 1915, **19**, 381); moreover, the form of the curves indicates that the change in

conductivity with dilution is not wholly due to electrolytic dissociation. It appears likely that there is a certain amount of hydrolysis of the compounds by the traces of water unavoidably present. Whether there is in addition an "alcoholysis," with the formation of sodium ethoxide, could not be determined, for dilute alcoholic solutions of sodium hydroxide and sodium ethoxide show practically the same conductivity.

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