131. *Effect of Solvents and Temperature on the Optical Rotation of Esters of Menthyl and Bornyl Hydrogen Xanthates, and on Menthyl and Bornyl Dixanthides.*

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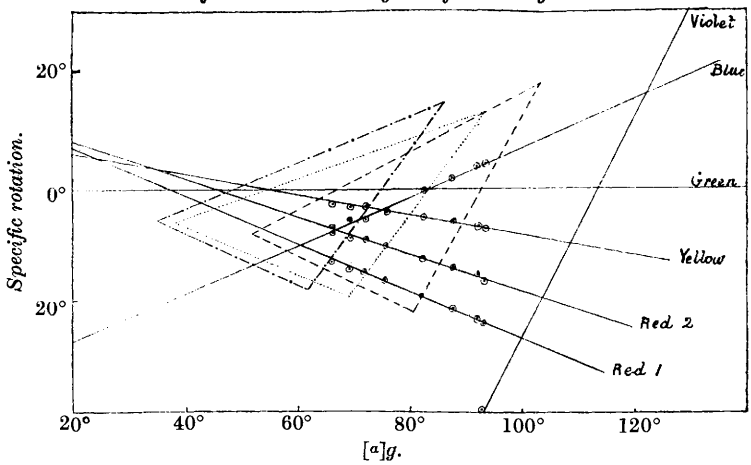
TSCHUGAEV (*Ber.*, 1909, **42**, 2244; *Z. physikal. Chem.*, 1910, **74**, 503) found that menthyl methyl xanthate, bornyl methyl xanthate, and the corresponding dixanthides in toluene solution showed anomalous rotation dispersion at high rotations. The methyl, *iso*propyl, benzyl, and *p*-nitrobenzyl esters of menthyl hydrogen

xanthate, bornyl methyl xanthate, and menthyl and bornyl dixanthides were therefore examined at laboratory temperatures in the usual solvents for six colours of light ranging from $\lambda = 6716$ to $\lambda = 4358$. Although the values for the specific rotations varied considerably with change of solvent, yet the rotation dispersion remained anomalous throughout. For the menthyl xanthates there is approximate similarity of order of effect of the different solvents. This order is reversed for bornyl methyl xanthate, and changes very considerably with the dixanthides.

The change of rotation with temperature in various solvents is small in all cases except those of menthyl benzyl xanthate and

FIG. 1.

Position of characteristic diagrams for menthyl xanthates.



———— *Menthyl methyl xanthate.*
— — — — *Menthyl* iso*propyl xanthate.*
. . . . . *Menthyl benzyl xanthate.*
—·—·—·— *Menthyl* p-*nitrobenzyl xanthate.*

menthyl *p*-nitrobenzyl xanthate. The latter ester in ethylene dibromide solution at 16° gives the only example of apparently simple rotation dispersion found in this work, the rotation becoming visibly anomalous above this temperature. All the curves are smooth, and show no maxima, minima, or points of inflexion.

Increase of concentration of menthyl methyl xanthate in pyridine solution at low temperatures diminishes the rotation, but increase of temperature causes the values to tend towards a common number.

The successive introduction of the *iso*propyl, benzyl, and *p*-nitrobenzyl groups into the xanthate molecule progressively reduces the rotation compared with the values obtained for the methyl ester, whereas formation of the dixanthide increases markedly the value

of the rotation. The latter holds also for the bornyl derivatives. The range of rotation observed for each substance in the different solvents is also similarly affected, and the characteristic diagrams for the different esters indicate very large regions of anomalous rotation dispersion, the diagrams being completely non-superimposable in spite of the fact that the variable group is not attached to the asymmetric carbon atom. One of these, that of menthyl methyl xanthate, is shown in full (see Fig. 1), the remainder of the diagrams for the menthyl xanthates being represented by the triangle enclosed by the lines $\lambda = 6716, 4916, 4358$ (red, blue, and violet), in order to avoid confusion. Further details regarding the various characteristic diagrams are given in the following table:

Substance.	Extent of anomalous region.	Value of $[\alpha]_{5461}$ at point of intersection of the green line with r_1.	r_2.	y.	b.	v.
Menthyl methyl xanthate	−6° to −122°	−37·5°	−46·0°	−55·0°	−83·0°	−113·0°
Menthyl *iso*propyl xanthate	0 to −103	35·5	42·5	45·5	67·0	92·5
Menthyl benzyl xanthate	−6·3 to −93·5	24·0	28·8	33·4	55·0	83·5
Menthyl *p*-nitrobenzyl xanthate	−19·0 to −85·0	23·2	25·5	26·0	48·5	74·8
Menthyl dixanthide	+5·6 to −402·0	42·0	33·0	74·0	173·0	308·0
Bornyl methyl xanthate	−14·0 to −130·0	20·0	22·3	29·0	54·3	101·8
Bornyl dixanthide	−6·7 to −150·0	25·5	18·2	6·7	71·5	128·4

Thus this group of substances appears to be unique because of the great size of the region of anomalous dispersion, and of the change in the characteristic diagram from substance to substance, whereas the menthyl esters of the nitrobenzoic and substituted nitrobenzoic acids (Kenyon and Pickard, J., 1915, **107**, 35) lie on one characteristic diagram with a small region of anomalous dispersion at $[\alpha]_{5461} = 55°$ to 70°, the remaining menthyl esters investigated lying on a diagram with little or no region of anomalous dispersion at the origin of rotation.

The individual data are given below.

Menthyl Methyl Xanthate.

In various solvents at 17°.

Solvent.	Conc.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
C_6H_6	5	−67·6°	−75·1°	−83·6°	−89·8°	−91·6°	−42·5°
EtOH	1·5	68·17	76·17	85·5	93·0	95·0	53·0
BuOH	2·0	66·6	74·00	83·62	88·50	89·87	39·95
C_5H_5N	5	69·0	77·4	84·68	91·90	93·8	47·3
$CHCl_3$	5	66·1	73·9	82·9	88·70	90·60	39·5
$C_2H_4Br_2$	5	57·6	63·4	70·3	72·3	66·68	+ 6·20
$C_6H_5{\cdot}NO_2$	5	66·4	73·4	80·8	87·6	89·4	−37·0
C_3H_7N	5	53·4	59·8	65·4	66·2	60·4	+17·40

In pyridine (p = 5·055).

Temp.	Density.	$[\alpha]_{r_2}$.	$[\alpha]_{r_1}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
12°	0·9927	−67·70°	−74·93°	−84·58°	−90·22°	−93·30°	−44·79°
26	0·9787	67·67	74·05	84·08	89·73	92·43	42·89
40·2	0·9646	67·50	73·94	83·24	89·27	92·02	41·21
57·8	0·9468	66·53	73·84	82·98	88·98	91·34	40·42
78·0	0·9265	66·00	73·61	82·30	88·03	91·23	39·71
97·0	0·9074	66·14	71·61	80·69	85·73	88·41	38·77

In pyridine (p = 20·00).

14·0	0·9972	65·54	73·85	82·06	87·68	89·39	36·88
30·5	0·9812	65·51	73·78	81·91	87·54	89·04	35·67
45·5	0·9666	64·90	73·22	81·42	87·05	88·56	34·96
59·2	0·9533	64·72	73·05	81·20	86·71	88·26	34·09
77·2	0·9363	64·13	72·74	80·98	86·38	87·78	33·29

In pyridine (p = 32·28).

13·5	1·0400	−63·76	−69·84	−77·48	−82·48	−82·47	−22·84
32·5	0·9855	64·20	72·05	80·00	85·20	86·00	30·08
46·0	0·9623	65·16	72·70	80·68	85·88	86·58	30·82
61·5	0·9471	64·63	72·43	80·60	85·71	86·09	31·52
79·0	0·9301	64·56	72·38	80·27	85·63	86·38	Unreadable

In ethylene dibromide (p = 4·825).

22·0	2·065	−59·06	−64·56	−70·58	−73·48	−68·18	+6·43
41·1	2·0278	59·80	64·93	71·03	74·27	68·88	4·36
58·0	1·9945	59·65	65·39	71·64	74·98	69·74	2·566
78·0	1·9548	60·22	65·92	72·54	75·86	71·02	−0·63
96·0	1·9240	60·33	66·03	72·42	76·24	71·94	5·29

In quinoline (p = 5·53).

14·5	1·0952	−52·91	−58·28	−62·67	−65·98	−59·10	+19·89
34·0	1·0795	53·56	59·00	63·89	66·96	59·98	16·79
45·0	1·0705	54·33	59·10	64·45	67·55	62·12	15·63
60·0	1·0585	54·65	59·78	65·12	68·18	63·76	14·55
78·0	1·0432	54·60	60·50	65·70	69·04	64·69	14·04
92·0	1·0316	55·31	61·03	66·29	69·50	65·12	13·50

Menthyl iso*Propyl Xanthate.*

In various solvents at 22·5°.

Solvent.	Conc.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
C_6H_6	5	−56·85°	−62·60°	−69·65°	−75·30°	−77·60°	−43·90°
BuOH	2	57·33	61·63	69·30	75·37	78·00	43·25
C_5H_5N	5	57·20	63·00	69·80	76·40	78·80	47·60
$CHCl_3$	5	55·20	61·60	68·80	74·10	75·80	41·80
$C_2H_4Br_2$	5	48·60	52·60	55·50	58·50	53·20	+ 2·00
$C_6H_5{\cdot}NO_2$	5	55·12	58·80	64·08	69·60	70·72	−28·20
C_9H_7N	5	47·00	51·40	54·80	57·40	52·40	+ 2·50

In ethylene dibromide (p = 5·091).

Temp.	Density.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
12·4°	2·066	−46·10°	−51·10°	−55·56°	−57·70°	−52·56°	+5·42°
31·0	2·030	46·82	51·95	56·84	59·00	54·65	3·677
47·3	1·999	47·44	52·86	57·57	59·93	56·20	0·295
63·0	1·967	47·94	53·43	58·42	61·40	57·90	−3·397
78·1	1·938	48·44	54·33	59·08	62·43	59·48	5·94
93·0	1·908	48·79	54·45	59·60	63·20	60·73	7·35

Menthyl Benzyl Xanthate.

In various solvents at 23°.

Solvent.	Conc.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
C_6H_6	5	−35·00	−38·73	−41·80	−43·50	−39·40	+ 9·20
BuOH	2	33·00	35·50	38·00	39·00	34·55	+19·75
C_5H_5N	5	35·00	37·90	40·90	42·82	39·00	+11·00
$CHCl_3$	5	35·00	38·98	41·85	43·05	38·60	+ 9·80
$C_2H_4Br_2$	5	27·40	30·28	30·26	30·34	21·92	+41·00
$C_6H_5{\cdot}NO_2$	5	29·60	31·80	32·80	33·30	25·80	+32·00
C_9H_7N	5	25·20	26·80	26·80	26·40	16·80	+47·20

In ethylene dibromide (p = 5·163).

Temp.	Density.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
11·0°	2·084	−25·65°	−27·06°	−28·06°	−26·85°	−15·78°	+47·48°
29·2	2·049	27·98	30·11	30·81	30·44	21·79	39·42
44·0	2·020	29·53	32·14	33·55	33·36	25·40	34·02
62·0	1·985	31·37	34·44	36·34	36·83	29·88	27·22
78·2	1·953	33·19	39·10	38·98	39·42	33·42	20·62
95·0	1·920	34·19	37·82	40·85	41·66	36·61	16·18

In benzene (p = 5·615).

13·0	0·8940	−34·45	−37·82	−40·84	−42·23	−38·01	+11·965
28·8	0·8777	36·33	40·38	44·03	46·26	42·40	4·06
43·5	0·8625	37·79	41·91	46·03	48·92	45·41	− 0·21
59·0	0·8460	39·15	43·78	48·12	50·94	49·45	5·89
75·0	0·8290	40·60	44·63	50·05	52·84	51·97	10·23

Menthyl p-*Nitrobenzyl Xanthate.*

In various solvents at 24°.

Solvent.	Conc.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
C_6H_6	5	−28·90°	−31·60°	−34·10°	−34·60°	−29·00°	+19·30°
BuOH	2	21·25	21·25	20·50	19·62	8·00	55·00
C_5H_5N	5	27·90	29·70	31·00	31·75	25·20	27·40
$CHCl_3$	5	25·15	27·80	28·10	28·60	20·00	34·70
$C_2H_4Br_2$	5	20·20	20·00	19·20	18·00	5·00	59·00
$C_6H_5{\cdot}NO_2$	5	21·90	22·30	21·90	21·32	10·32	Unreadable
C_9H_7N	5	23·60	24·40	24·30	24·00	15·60	44·40

In ethylene dibromide (p = 5·046).

Temp.	Density.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
16·3°	2·084	−19·81°	−18·44°	−17·04°	−15·84°	− 2·69°	+62·73°
29·3	2·060	21·84	22·09	21·33	20·38	9·093	54·84
44·0	2·033	23·73	24·71	24·92	24·38	14·07	45·99
59·0	2·003	25·79	27·46	28·11	27·79	18·80	37·94
75·0	1·971	27·98	30·00	31·25	31·51	24·04	29·16
91·5	1·938	29·69	32·42	34·59	34·94	27·95	21·52

In benzene (p = 5·555).

18·0	0·8933	−29·93	−32·54	−34·45	−35·96	−30·73	+15·52
31·5	0·8790	30·52	33·93	36·66	38·29	33·67	10·44
46·0	0·8628	31·51	35·16	38·19	40·27	36·37	7·095
60·0	0·8480	32·58	36·84	40·34	42·04	38·34	2·76
73·5	0·8334	32·92	37·78	41·00	43·31	41·36	0·216

Menthyl Dixanthide.

In various solvents at 22°.

Solvent.	Conc.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
C_6H_6	5	−175·0°	−203·5°	−234·1°	−259·9°	−294·1°	−217·7°
EtOH	0·5	229·0	278·0	312·0	342·0	412·0	376·0
BuOH	2	214·5	254·0	291·0	318·5	376·5	322·5
C_5H_5N	5	176·2	203·0	236·6	262·5	291·6	214·5
$CHCl_3$	5	219·4	253·4	291·6	326·6	384·2	358·0
$C_2H_4Br_2$	5	221·0	255·4	293·2	327·8	390·6	343·6
$C_6H_5{\cdot}NO_2$	5	177·0	204·6	233·8	256·6	291·0	206·0
C_9H_7N	5	149·2	170·8	197·2	216·8	233·6	126·0

In benzene (p = 5·598).

Temp.	Density.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
12·7°	0·8954	−182·4°	−208·8°	−238·1°	−261·7°	−298·6°	−213·4°
28·2	0·8790	182·4	208·5	238·1	263·9	301·8	216·3
41·2	0·8654	182·5	209·4	238·7	264·3	301·2	220·8
58·0	0·8482	182·9	210·9	240·8	266·1	303·5	220·8
69·0	0·8362	182·6	210·9	240·9	266·7	303·9	220·8

In chloroform (p = 5·104).

13·5	1·459	−227·9	−262·9	−298·9	−335·1	−395·8	−371·3
30·7	1·428	222·7	254·5	293·2	327·7	385·5	354·9
41·8	1·407	219·6	250·5	290·4	324·6	380·2	345·7
55·7	1·392	213·3	245·4	283·1	317·6	370·5	332·8

Bornyl Methyl Xanthate.

In various solvents at 17°.

Solvent.	Conc.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
C_6H_6	5	−29·2°	−31·5°	−34·6°	−35·8°	−30·0°	+18·0°
EtOH	1·5	32·67	35·33	39·00	40·33	35·67	− 0·33
BuOH	2·0	31·75	35·00	40·75	41·00	35·67	− 0·75
C_5H_5N	5	27·2	29·6	31·0	31·1	25·4	+24·00
$CHCl_3$	5	33·4	36·5	41·5	42·3	39·1	+ 2·7
$C_2H_4Br_2$	5	37·05	40·4	46·5	49·0	47·2	− 6·7
$C_6H_5{\cdot}NO_2$	5	38·4	43·4	50·2	52·4	54·6	−23·8
C_9H_7N	5	29·90	33·00	36·00	37·6	33·4	+ 8·4

In pyridine (p = 5·012).

Temp.	Density.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
14·0°	0·9951	−27·32°	−29·84°	−31·65°	−32·09°	−26·08°	+25·30°
32·0	0·9751	25·39	28·00	29·59	29·78	22·44	28·61
48·0	0·9390	24·06	26·97	27·77	27·83	20·48	31·08
61·5	0·9455	22·95	25·00	26·13	25·86	18·07	33·54
78·8	0·9280	21·60	23·32	24·49	23·66	15·75	36·68
93·0	0·9137	20·51	22·01	22·59	22·25	13·78	38·49

In ethylene dibromide (p = 5·274).

7·7	2·092	−38·02	−42·62	−47·31	−50·04	−48·93	− 9·27
27·7	2·053	35·30	39·18	42·89	45·12	43·01	1·033
44·3	2·0215	32·89	36·12	39·57	41·33	38·19	+ 5·51
57·3	1·9955	31·07	34·07	37·25	38·37	34·40	10·04
77·8	1·9555	27·94	30·85	33·05	33·95	28·81	17·61
95·3	1·9220	25·54	28·13	29·94	30·18	24·30	Unreadable

In quinoline (p = 4·997).

14·0	1·0974	−31·11	−34·30	−36·48	−38·17	−33·05	+10·05
34·0	1·0820	29·83	32·60	34·34	35·60	30·69	16·47
51·3	1·0688	26·45	30·25	32·03	33·00	26·10	20·59
65·8	1·0575	25·43	28·30	30·76	30·76	24·31	23·90
81·5	1·0452	24·90	27·29	28·90	28·50	21·91	27·17
94·0	1·0355	24·16	26·22	26·93	26·58	20·77	Unreadable

Bornyl Dixanthide.

In various solvents at 22°.

Solvent.	Conc.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
C_6H_6	5	−36·30°	−39·60°	−41·98°	−45·60°	−38·00°	+44·90°
EtOH	1	57·50	65·00	72·00	79·00	81·00	−22·77
BuOH	2	56·00	64·50	72·00	77·00	79·00	20·00
C_5H_5N	5	39·40	43·00	45·60	48·60	42·60	+35·20
$CHCl_3$	5	54·7	64·00	70·20	75·30	76·30	−17·50
$C_2H_4Br_2$	5	40·60	44·20	49·10	51·80	46·40	+30·20
$C_6H_5{\cdot}NO_2$	5	50·00	57·80	64·20	69·20	68·00	− 6·00
C_9H_7N	5	44·00	51·40	56·20	59·20	57·00	+15·20

In benzene (p = 5·54).

Temp.	Density.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
12·6°	0·8968	−36·68°	−40·35°	−43·53°	−44·54°	−38·00°	+46·22°
27·0	0·8816	37·31	42·24	45·31	47·21	39·81	41·28
45·8	0·8626	38·65	43·52	47·00	49·09	42·16	39·96
55·8	0·8532	39·43	44·00	48·59	49·46	43·09	37·48
72·0	0·8364	39·50	44·17	48·48	50·10	43·57	36·67

In chloroform (p = 5·088).

11·5	1·476	−55·23	−63·23	−69·88	−76·34	−78·97	−23·29
30·8	1·441	54·43	61·35	69·34	75·10	77·28	18·06
43·8	1·417	54·77	61·94	68·77	73·97	74·67	13·25
55·0	1·397	54·14	60·94	67·73	73·35	73·35	12·20

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