JOURNAL
OF
THE CHEMICAL SOCIETY.

TRANSACTIONS.

I.—*Influence of Temperature on the Refractive Power
and on the Refraction Equivalents of Acetylacetone
and of Ortho- and Para-toluidine.*

By W. H. PERKIN, Ph.D., F.R.S.

IN 1892, I communicated to the Society a description of an apparatus for determining the refractive power of compounds at different temperatures, together with some results obtained by its use (Trans., 1892, **61**, 287). In two later communications, an account was given of the magnetic rotation of substances supposed to contain acetyl, or to be of ketonic origin (Trans., 1892, **61**, 800, and 1894, **65**, 815); in these it was shown, from their magnetic rotations, that some di- and tri-ketonic compounds are tautomeric, and that when heated they change in varying degrees from their hydroxylic, or unsaturated form, to their saturated, or ketonic form, the rotations becoming lower in consequence. The refractive power of several of these compounds was also taken at different temperatures, showing changes in reference to this property, of the same order as in the case of the rotations; this was expected because it has been shown (Gladstone and Perkin, Trans., 1889, **55**, 750) that there is an analogy in most cases between the variations in the rotation and refraction of the same compounds.

Among the substances examined, acetylacetone, methylacetylacetone, allylacetylacetone, and diacetylacetone were shown to undergo internal change, in the most striking manner, by change of temperature.

Since the account of these experiments was published, Brühl, in his

interesting paper entitled a "Study of Tautomerism," gives the results he obtained on the refractive power of acetylacetone at temperatures wide apart; the numbers, however, do not agree with mine, and the same is the case with some of his more recent measurements of the refractive power of para- and ortho-toluidines (*Zeit. phys. Chem.*, 1895, **16**, 216). Knowing the great care Professor Brühl takes in making his determinations, I have been induced to repeat my measurements of acetylacetone and the two toluidines, to see if any error could be discovered in the previous work, or any other explanation found of these discrepancies, for it is of great importance from a theoretical point of view to find out whether the analogy between the refraction and magnetic rotation of the di- and tri-ketonic and other compounds, which my results are supposed to indicate, exists or not.

In all my determinations, I have used the apparatus described in this Journal a few years ago (*Trans.*, 1892, **61**, 288), which is simply a hollow prism containing the substance under examination, heated in an air bath. In making the observations, readings were invariably taken from both sides of the prism, and the sum of the result divided by two, so that if any slight shifting of the zero took place during the raising of the temperature (which, however, does not appear to occur) it would not influence the result.

I understand from Professor Brühl that in his determinations of the refractive power of acetylacetone, and I presume also in that of the toluidines and other substances, where temperatures above that of the atmosphere are employed, he used the total refractometer which he has described (*Ber.*, 1891, **24**, 286).

The following results were obtained with acetylacetone. The specimen employed was that given to me by Professor Claisen, and referred to in the *Transactions* (1892, **61**, 844) as Specimen II. The first set of results marked "A," given below, were made some time since, the product being previously distilled under the ordinary pressure. The other three, marked "B," were obtained quite recently; for these the acetylacetone was redistilled under reduced pressure the day before it was examined, and, as the specimens were not quite identical, the results have been kept separate. For the purposes of this paper it will only be necessary to give the numbers for the three hydrogen lines.

	A.		B.					
Line <i>t.</i>	<i>t.</i>		<i>t.</i>	<i>t.</i>	<i>t.</i>	<i>t.</i>		
H _α	15.5°	1.44930.	6.5°	1.45459.	8°	1.45390.	9.5°	1.45270.
H _β	15.5°	1.46718.	6.5°	1.47259.	8°	1.47200.	9.5°	1.47053.
H _γ	15.5°	1.47939.	6.5°	1.48524.	8°	1.48451.	9.5°	1.48315.

Densities—

“A.” $d_{15.5^\circ/4^\circ}$ 0.9800.“B.” $d_{6.5^\circ/4^\circ}$ 0.9871. $d_{8^\circ/4^\circ}$ 0.9862. $d_{9.5^\circ/4^\circ}$ 0.9827.Molecular refraction $\frac{\mu - 1}{d}p$.

A.			B.					
H _α	15.5°	45.807.	6.5°	46.041.	8°	46.026.	9.5°	46.060.
H _β	15.5°	47.629.	6.5°	47.874.	8°	47.861.	9.5°	47.871.
H _γ	15.5°	48.875.	6.5°	49.155.	8°	49.129.	9.5°	49.167.

The following are the results obtained at higher temperatures.

A.		B.	
H _α	99.2° 1.40210.	99.0°	1.40240.
H _β	99.2° 1.41604.	99.0°	1.41656.
H _γ	99.2° 1.42555.	99.0°	1.42605.

Densities—

 $d_{99.2^\circ/4^\circ}$ 0.8975. $d_{99^\circ/4^\circ}$ 0.8960.Molecular refraction $\frac{\mu - 1}{d}p$.

A.		B.	
H _α	99.2° 44.802.	99°	44.908.
H _β	92.2° 46.355.	99°	46.488.
H _γ	99.2° 47.415.	99°	46.547.

Relationship of Results.

A.				
15.5°	H _α 45.807.	H _β 47.629.	H _γ 48.875.	
99.2°	H _α 44.802.	H _β 46.355.	H _γ 47.415.	
Diff.	83.7	1.005	1.274	1.460
B.				
Av. 8°	H _α 46.042.	H _β 47.869.	H _γ 49.150.	
99°	H _α 44.908.	H _β 46.488.	H _γ 47.547.	
Diff.	91°	1.134	1.381	1.603

The results already published, obtained by the examination of the acetylacetone, given to me by Professor Dunstan (Trans., 1892, 61, 840, 847), called “Specimen I,” although represented by slightly lower numbers than those given above, exhibited very similar differences for variations of temperature. For 88.3° they are 1.103,

1·341, 1·551 respectively, these and the above calculated for 100°, give—

	H _α .	H _β .	H _γ .
A	1·200	1·522	1·744
B	1·246	1·517	1·761
Spec. I....	1·249	1·518	1·756
Average diff.	1·232	1·519	1·754

These differences are as close to each other as could be expected, and show that the results obtained with my instrument are very regular; these vary, however, with the line taken for comparison, that for H_γ being considerably larger than that for H_α, showing that the *dispersion* as well as the refraction diminishes with rise of temperature.

The fresh results given above are therefore seen to be in close agreement with those previously published.

The numbers obtained by Brühl for acetylacetone (*J. pr. Chem.*, 1894, **50**, 190), and compared with the above, corrected for temperature by the coefficient 1·232 for 100°, are as follows.

	Brühl.	Perkin.
8°	—	46·04
16·7°	45·95	45·93
18·0°	45·90	45·92
42·7°	46·33	45·61
72·4°	46·66	45·25

It will be seen that the numbers given for the temperatures 16·7° and 18° are very nearly the same in both columns, but directly temperatures much above the atmospheric are employed Brühl's numbers rise, whereas mine fall; and this rise is very considerable, being about 0·71 for 55·7°, or about 1·27 for 100°. That the refractive power of a substance should increase in this manner is a result which would not be anticipated.

The two toluidines, ortho- and para-, being stable substances and unlike acetylacetone not changing in structure when heated, are useful for the purpose of comparison. Paratoluidine, however, being solid, and not fusing until about 43° could not, of course, be examined in a pure condition below that temperature, it was, therefore, compared side by side with orthotoluidine at about 49°. The following are the numbers obtained, those given for paratoluidine being the average of three closely concordant sets of determinations made at different periods.

	<i>t</i> .	H _α .	H _β .	H _γ .
Paratoluidine	49·6°	60·642	63·129	64·741
Orthotoluidine....	49·0°	60·585	63·028	64·632
Diff.	—	0·057	0·102	0·109

In passing, attention may be drawn to the fact that these differences increase in magnitude with the more refrangible rays, being greatest for H_{γ} . This indicates a slight difference in the dispersion of the two substances, that of the ortho-compound being the smaller of the two.

Determinations were then made of a solution of paratoluidine in orthotoluidine in molecular proportion, that is, equal weights; also of the orthotoluidine used in making this mixture. The following are the results.

Densities—

Mixture	d	$10^{\circ}4'/4^{\circ}$	1.0005	
Orthotoluidine ..	d	$9^{\circ}7'/4^{\circ}$	1.0074	
	$t.$	$H_{\alpha}.$	$H_{\beta}.$	$H_{\gamma}.$
Mixture	$10^{\circ}4'$	1.56745	1.59067	1.60589
Orthotoluidine .	$9^{\circ}7'$	1.57110	1.59415	1.60943

Molecular refraction.

	$H_{\alpha}.$	$H_{\beta}.$	$H_{\gamma}.$
Mixture	121.366	126.333	129.588
Orthotoluidine.....	60.658	63.106	64.729
Paratoluidine	60.708	63.227	64.857
Differences between the two toluidines	0.050	0.121	0.128

These differences are very close to those obtained at 49° . It is seen from these results that the ortho-compound gives lower numbers, indicating the same variation in dispersion. The refractive power of the bases is also very similar, but slightly lower at the higher temperature; this has been shown to be invariably the case with all substances yet examined by my apparatus.

Brühl's numbers for paratoluidine at 59.1° give H_{α} 61.575 and for H_{γ} 65.459, results which are much higher than mine, and also much higher than he obtained for orthotoluidine at 20° . The latter are practically the same as those obtained in my experiments at 9.7° , thus—

Brühl.	Perkin.
20° 60.70	9.7° 60.658

In the case of the toluidines, therefore, Brühl's results increase as the temperature rises, whilst mine fall very slightly; in fact, wherever Brühl has examined a substance at two widely different temperatures the same fact is observed, thus, in the case of ethylic monocarboxethylacetoacetate, at 21.1° , 81.319 is obtained, but at 70.8 , 82.920, and for methylformylcamphor, at 23.1° , 95.191, but at 47.3° , 96.072. These numbers are for $\frac{\mu x - 1}{d} p$.

6 INFLUENCE OF TEMPERATURE ON THE REFRACTIVE POWER.

As our results agree closely at ordinary temperatures, but differ at higher temperatures, there can be no doubt that the want of accord between our determinations is due to the different instruments we employ. The question then is which is to be taken as giving correct results?

With reference to the apparatus employed in my determinations, one cannot see any reason why a hollow prism, filled with the substance under examination, should not give as good results at 100° as at 15°.

There has not been very much work done by others on the refractive power of compounds at widely different temperatures, the most important being that of Nasini and Bernheimer (*Gazzetta*, 1885, **15**, 59) and (*Jahrsber.*, 1885, 314), who used a hollow prism, heated by passing hot water through the jacket by which it was almost entirely surrounded. With this they obtained results similar to mine, showing that, in the case of stable compounds such as they examined, the molecular refraction does not alter very much with temperature, although it becomes somewhat smaller. The following are examples

	$t.$	$\frac{\mu_a - 1}{d} p.$	$t.$	$\frac{\mu_a - 1}{d} p.$
Dimethylnaphthalene	16·4°	93·11	77·7°	92·73
Bromonaphthalene ..	16·5°	90·54	77·6°	90·50
Methylnaphthol	13·9°	88·59	77·7°	88·32
Cinnamic alcohol. ...	24·8°	73·83	77·3°	73·59
Anethöl	14·9°	82·95	77·3°	82·66

This reduction has been shown to vary with different classes of compounds (*Trans.*, 1892, **61**, 308), and is apparently of the same kind as the temperature differences observed in connection with magnetic rotations.

The agreement in the results obtained with the instrument used by Nasini and Bernheimer and with mine shows that not only the hollow prism, but also that the optical arrangements in both cases, although not identical, acted in the same manner; and, what is more important, the results obtained by Kettler, in his determinations of the refractive power of water, agree closely with mine (*Trans.*, 1892, **61**, 293), although he used an entirely different instrument containing no prism (*Ann. Phys. Chem.*, 1888, **33**, 28). It would seem, therefore, that there must be some unnoticed source of error in the refractometer used by Brühl, when it is employed for temperatures somewhat above those of the atmosphere.