suggested on the basis that it is compatible with ideas on the radiocolloidal properties of scandium in low concentrations[21] and that the observed log–log relationship can be arrived at by a theoretical treatment of a reaction of the type

$$Sc^{+3} + nH_2O \rightleftarrows Sc(OH)_n^{3-n} + nH^+$$

and the assumption of the adsorption of the hydroxy form of the scandium. An alternate explanation is competition between scandium(III) ions and the hydrogen ion for sites on the adsorbent.

Figure 3 shows adsorption–concentration relationships for scandium on charcoal in the presence of 0.1 *N* perchloric acid. The value of these observations is that they indicate a useful approach for obtaining the concentrations of unknown solutions of tracer scandium. The deviations from Henry's law in this case might be assigned to the adsorption of hydroxy forms of scandium, or since the acid anion affects adsorption, it might be referred to competitive complex formation.

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[21] G. K. Schweitzer and W. M. Jackson, *J. Chem. Educ.*, **29**, 513 (1952).

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A Comparative Study of Methyl Compounds of the Elements

BY R. T. SANDERSON

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Thirty-four elements, representing all the active major groups of the periodic table, are known to form methyl compounds of the type, $E(CH_3)_n$.[1] Most of these have covalently bound methyl groups in which there are no unshared electrons or unoccupied low energy orbitals. The methyl compounds as a group thus present a unique opportunity for observing, with a minimum of ambiguity, the relationships among physical and chemical properties and atomic charges associated with bond polarities.

Partial charges on the atoms of all known (and a few other) methyl element compounds have been estimated by methods recently described.[2] The net charges on methyl (the sum of charges on carbon and hydrogen), together with an outline of some properties of the methyl compounds, are presented in Table I. The order is of decreasing negative and increasing positive net charge on methyl. This is equivalent to the order of progressive change in polarity of the C–E bonds.

Physical State.—All methyl compounds of the elements in which the net negative charge on methyl exceeds −0.25 are solids. Where the change is −1.00, and possibly even where it would exceed −0.40, the solids are non-fusible and generally insoluble, appearing to be polymeric. Evidence of association diminishes with decreasing negative charge on methyl. All the rest are volatile and most beyond Mg and Be are liquids or gases. In no compound with charge on methyl less than −0.17 is there evidence of vapor phase association.

TABLE I

POLARITY AND PROPERTIES OF METHYL COMPOUNDS

Element	Net charge on CH_3	Physical state[a]	Spontaneous reactivity[b] with O_2	CO_2	H_2O
Cs	−1.000	S, NV	r	r	r
Rb	−1.000	S, NV	r	r	r
K	−1.000	S, NV	r	r	r
Na	−1.000	S, NV	r	r	r
Li	−1.000	S, NV	r	r	r
Ba	−0.479	(known only in complex soln.)			
Sr	− .452				
Ca	− .416				
Mg	− .325	S, V	r	r	r
Be	− .250	S, V	r	r	r
Al	− .170	L	r	r	r
Cd	− .131	L	r	n	s
Zn	− .095	L	r	n	s
B	− .067	G	r	n	n
Si	− .067	L	n	n	n
In	− .065	S, V	s	n	s
Sn	− .032	L	n	n	n
Ga	− .031	L	r	n	s
P	− .023	L	r	n	n
Sb	− .019	L	r	n	n
Hg	− .016	L	n	n	n
H	− .012	G	n	n	n
Tl	− .002	S, V	r	n	s
Ge	− .001	L	n	n	n
Te	.002	L	s	n	n
Pb	.004	L	n	n	n
C	.010	G	n	n	n
Bi	.013	L	s	n	s
As	.023	L	s	n	n
I	.046	L	n	n	n
S	.053	L	n	n	n
N	.062	G	n	n	n
Se	.067	L	n	n	n
O	.151	G	n	n	n
Br	.170	G	n	n	n
Cl	.235	G	n	n	n
F	.357	G	n	n	n

[a] S = solid, L = liquid, G = gas, V = volatile, NV = non-volatile. [b] r = rapid, s = slow, n = very slow or none.

Oxidation.—Oxidation by oxygen appears to be related to atomic charges and also to availability of low energy orbitals. All methyl compounds having net negative charges on methyl greater than about −0.07, and also, presumably, an unoccupied low energy orbital, are spontaneously inflammable in air. When the orbital is available (as in B, Al, Ga, In, Tl, P, As, Sb, Bi), apparently whether or not it contains electrons, even smaller net negative charges on methyl appear sufficient for easy oxidation, although not always spontaneous inflammation. When the orbital is not available (as in Si, Ge, Sn, Pb), the compound appears relatively stable toward oxidation. Incidentally, the Group V alternations previously explained[3] are to be

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[1] See N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, New York, N. Y., 1950, for references to the original literature.

[2] R. T. Sanderson, *J. Chem. Educ.*, **32**, 140 (1955).

[3] R. T. Sanderson, THIS JOURNAL, **74**, 4792 (1952).

noted here: methyl compounds of the less electronegative P and Sb are spontaneously inflammable but those of the more electronegative As and Bi are not.

Oxidation by carbon dioxide occurs readily for the compounds with most negative methyl but is slight or negligible where the charge on methyl is less than −0.15.

Hydrolysis.—As might be expected, hydrolysis of methyl compounds capable of both reaction with carbon doxide and spontaneous inflammation in air is violent. As the charge on methyl becomes less than −0.07, only the methyl compounds of Ga, In and Tl are appreciably susceptible to attack by water, and these, stepwise, the intermediates being stable. It is evidently necessary to provide an unoccupied orbital. The unreactivity of the boron compound seems somewhat anomalous and may be associated with steric effects.

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The Long Wave Photochemistry of Biacetyl and its Correlation with Fluorescence at Temperatures over 100°

BY GEORGE F. SHEATS[1] AND W. ALBERT NOYES, JR.

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A study of the photochemistry of biacetyl at 4358 and at 3650 Å. has recently been published.[2] Primary quantum yields were calculated by an equation based on the mechanism of Bell and Blacet.[3] This equation seems satisfactory at temperatures below 100°. At temperatures over 100° the primary quantum yield should be equal to the ethane yield if acetyl radicals and $CH_2COCOCH_3$ radicals dissociate completely.[3] However, the primary yield calculated by equation 14 of the previous paper and the ethane yield do not agree. They should agree if the mechanism is correct and complete. This indicates that steps other than those in the mechanism occur, in agreement with recent findings of Guenther, Whiteman and Walters[4] on the thermal reaction.

It is certain that the primary yield is greater than the ethane yield and it may be below the value calculated by equation 14 of the previous article. Formation of $CH_3COCOCH_2CH_3$ would not vitiate the calculations by equation 14. On the other hand, $(CH_3)_2COHCOCH_3$ or $(CH_3)_2C(OCH_3)COCH_3$ formed from the possible intermediate radical $(CH_3)_2COCOCH_3$[5] would mean that the primary yield is less than that calculated by equation 14. Formation of any of these compounds including $CH_3COCOCH_2CH_3$ would make the primary yield greater than the ethane yield.

Equation 14 should give approximately correct values of the primary yield, although discrepancies may increase with increase in temperature. This equation is used and certain tentative conclusions about the relationship of fluorescence to primary photochemical process are drawn.

Experimental

The apparatus and analytical procedure were the same as those described previously.[2]

Monochromatic light at 4358 Å. was obtained by a combination of Corning Glasses 3389 (2.5 mm.) and 5113 (2.0 mm.). Radiation at 3650 Å. was obtained by Corning Glass 5860 (5.0 mm.). Less than 1% of radiation at 3340 Å. was present. General Electric Company AH.6 mercury arcs were used. The beam completely filled the reaction vessel. Intensity was varied by chrome–alumel neutral density filters.[6]

Results

The results are given in Table I. The primary quantum yields in the sixth column are calculated from equation 14 of the previous article.

The revised activation energy for methane formation given by Ausloos and Steacie[7] has been used to calculate the acetone yield. This calculation would be in error if other compounds than the ones given in the mechanism of Bell and Blacet[3] are formed.

TABLE I

QUANTUM YIELDS FROM BIACETYL AT 4358 AND 3650 Å. AT TEMPERATURES OVER 125°

Cell, 2.3 cm. × 20.0 cm.; temperatures are controlled to about ±1°.

(B) Biacetyl concn. molecules $\times 10^{-17}$/ml.	I_a, quanta $\times 10^{-12}$ absorbed/ml./sec.	Φ_{CO}	$\Phi_{C_2H_6}$	Φ_{CH_4}	ϕ	$\frac{R_{CH_4}}{R^{1/2}_{C_2H_6}(B)} \times 10^{12}$ molecules$^{-1/2}$ ml.$^{1/2}$ sec.$^{-1/2}$
		4358 Å., 125°				
9.40	117	0.23	0.057	0.032	0.12	1.6
10.2	119	.20	.052	.029	.10	1.4
		4358 Å., 145°				
9.90	47.3	0.41	0.080	0.092	0.18	2.2
9.86	361	.40	.12	.046	.21	2.5
		4358 Å., 174°				
10.0	45.1	0.84	0.14	0.27	0.30	4.8
		4358 Å., 198°				
10.4	4.74	1.52	0.070	0.73	0.42	5.8
9.77	43.0	1.28	.17	.46	.45	7.3
9.59	104	1.00	.16	.32	.39	8.3
9.55	334	.85	.20	.20	.37	8.3
		3650 Å., 124°				
2.98	13.8	0.64	0.22	0.054	0.35	1.5
5.61	17.6	.53	.15	.074	.26	1.4
8.31	37.9	.50	.14	.069	.25	1.4
11.9	17.5	.48	.094	.12	.19	1.4
		3650 Å., 198°				
2.32	13.5	1.08	0.24	0.28	0.45	9.0
5.29	17.3	1.23	.17	.44	.44	8.4
10.2	14.7	1.57	.13	.70	.45	7.3

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[1] Hanovia Chemical and Manufacturing Company Predoctoral Fellow during 1953–1954. This work was supported in part by contract with the Office of Naval Research, United States Navy.

[2] G. F. Sheats and W. A. Noyes, Jr., THIS JOURNAL, **77**, 1421 (1955).

[3] W. E. Bell and F. E. Blacet, *ibid.*, **76**, 5332 (1954).

[4] W. B. Guenther, C. A. Whiteman and W. D. Walters, *ibid.*, **77**, 2191 (1955).

[5] B. de B. Darwent, *Discs. Faraday Soc.*, No. 14, 129 (1953).

[6] See R. Gomer and W. A. Noyes, Jr., THIS JOURNAL, **71**, 3390 (1949).

[7] P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 39 (1955).