

On the Exchange of Cyanide with Nitriles

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Citation: *The Journal of Chemical Physics* **17**, 585 (1949); doi: 10.1063/1.1747334

View online: <http://dx.doi.org/10.1063/1.1747334>

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used by Rittenberg, Bleakney and Urey⁷ in determining equilibrium at 468°C; however, with 35± percent H₂ the correction is less important. Their results produce an average $K_{468^\circ\text{C}}$ of 3.75 ± 0.07 , as compared to the theoretical value of 3.82.

* Rate measurements were made in eight minutes or less to minimize possible diffusion separation; linearity of the semilog plots of diffusion rates indicated that separation, if any, was negligible.

¹ Wender, Friedel, and Orchin, *J. Am. Chem. Soc.* (in press).

² N. Bauer, and J. Y. Beach, *J. Chem. Phys.* **15**, 150 (1947).

³ D. P. Stevenson, *J. Chem. Phys.* **15**, 409 (1947).

⁴ R. Honig, *J. Chem. Phys.* **16**, 837 (1948).

⁵ Kindly supplied by Dr. J. Kummer, Mellon Institute.

⁶ Wooley, Scott, and Brickwedde, *J. Res. N. Bur. Stand.* **41**, 379 (1948).

⁷ Rittenberg, Bleakney, and Urey, *J. Chem. Phys.* **2**, 48 (1934).

On the Exchange of Cyanide with Nitriles

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April 7, 1949

THE existence of exchange equilibria between free cyanide ion and the -CN group of nitriles has been reported in the case of beta-hydroxy propionitrile which is claimed to exchange its nitrile carbon with cyanide to the extent of a few percent of equilibrium exchange when maintained under alkaline conditions at 100°C for one hour in the presence of approximately equimolar amounts of cyanide labeled with the 21-min. carbon isotope C¹¹.¹ Aside from its theoretical interest, this observation implies that a variety of carboxylic acids labeled in the carboxyl group could be synthesized merely by exchanging the appropriate nitrile with labeled cyanide, separating the nitrile, and hydrolyzing to the corresponding acid. We have re-investigated the exchange properties of beta-hydroxypropionitrile under a variety of conditions and in addition have extended our observations to methyl, phenyl, and succinyl cyanides. The following is a preliminary report of the procedures followed and results obtained.

A stock solution of labeled sodium cyanide** in distilled water was prepared which upon precipitation as AgCn exhibited an activity of 8400 ± 100 ct/min. assayed in thick sample geometry with a RCL nucleometer. The assay technique was reproducible to within ± 3 percent on many duplicate standard samples. In all experiments, nitrile in a large molar excess was added to a convenient amount of the labeled cyanide solution and brought to the desired acidity or alkalinity with HNO₃. Under these conditions, any appreciable exchange occurring would be indicated by a marked decrease in the specific activity of the cyanide. The corresponding specific activity of the nitrile following exchange could be calculated and compared with that observed. In addition, the recovery of total activity was checked. In calculating the activity to be expected, account was taken of the difference in carbon content of the various silver salts compared to silver cyanide. All samples were corrected to a standard thickness whenever the amounts collected were insufficient to give a true "infinite" thickness. The area of precipitate (2.26 sq. cm) was constant in all cases cited in this report.

In Table I, the results of the experiments with the one aromatic and two aliphatic unsubstituted nitriles are shown. It is seen that under the conditions noted there was no exchange between the organonitrile group and the free cyanide.

The experiments with beta-hydroxy propionitrile were carried out in acid, slightly alkaline and alkaline media, again with a large excess of the nitrile to enhance any change in specific activity of the cyanide consequent upon exchange. The procedure employed in the early experiments¹ involved alkaline distillation of the nitrile. This procedure did not appear adequate to prevent traces of cyanide from contaminating the nitrile. The procedure finally adopted involved precipita-

TABLE I. Exchange experiments with unsubstituted nitriles.

Experimental conditions†	Separation procedure	Percent random exchange
3.5 ml 0.5 M NaC* N 0.5 ml CH ₃ CN 5 ml N NaOH in 10 cc H ₂ O. Heated for two hours at 75°C	Cooled, cyanide ppt with Ag+ in dil. HNO ₃ Filtrate acidified with conc. H ₃ PO ₄ (1 vol. H ₃ PO ₄ :1 vol. filtrate). Refluxed 4 hrs., resultant acetic acid distilled and collected as AgC ₂ H ₃ O ₂	<0.5 percent
0.5 M NaC* N 1 ml C ₆ H ₅ CN 1 ml 5N NaOH dil. 1:1 with alcohol, brought to final vol. 50 cc with dist. H ₂ O. Heated one hour at 75°C	Cyanide precipitated with Ag+ in dilute HNO ₃ Filtrate hydrolyzed with conc. NaOH, solution acidified, benzoic acid separated by crystal- lization	<0.08 percent
1 ml 0.5 M NaC* N 1 ml N NaOH 200 mgm (CH ₃) ₂ (CN) ₂ brought to final vol. 10 cc with dist. H ₂ O. Heated in boiling water 1 hr.	Nitrile extracted with chloroform, after precipi- tation of cyanide in dil. acid solution	<0.3 percent

† The asterisk (*) denotes labeled carbon.

tion of the cyanide in dilute acid, followed by extraction under alkaline conditions of the residual nitrile with chloroform. Control experiments in which unlabeled cyanide was mixed with a large excess of nitrile showed quantitative recovery of the cyanide to be possible by this procedure.

Incubation of the cyanide with 20-fold molar excess nitrile under acid conditions followed by separation of cyanide and nitrile revealed no change in the specific activity (<0.5 percent) random exchange. Under alkaline conditions (pH 9-14), the specific activity of the cyanide was observed to drop from 8400 to an average value of 7700 (see Table II). From this figure alone one could calculate 9.2 percent randomization of the cyanide with nitrile. However, the recovery of activity in the separated nitrile was 10-fold too high for the amount of specific activity loss observed for the cyanide. Furthermore it proved impossible to precipitate the cyanide completely (Table II) once it had been allowed to interact with the nitrile at 75°C or 100°C for one or two hours. The basis for this behavior is not known. Presumably complex formation or reaction of the reagents, or hydrolysis products thereof, could account for the observed incompleteness of cyanide recovery, as well as for the disproportionation in specific activity of nitrile and cyanide. The possibility that labeled formate formed by hydrolysis was reacting with the nitrile or its hydrolysis products has been excluded in control experiments with unlabeled formate. This matter is being investigated further.

TABLE II. Change in specific activity of cyanide in experiments with beta-hydroxy propionitrile.

Experimental conditions	Wt. of Ag CN ppt. (mgm)	Specific activity†	Standard specific activity
A. 1 ml 0.5N NaCN, 0.6 ml beta-hydroxy propionitrile (dist.), HNO ₃ to final vol. 10 cc (0.1N HNO ₃). Heated at 100°C for 1 hr.	57.2	8250	8400
B. as in A but no acid or alkali added	32.3	8300	8400
C. as in A, but 0.1N in NaOH	19.1 18.2	7710 7700	8400
D. as in A, but 0.5N in NaOH	34.6 35.6	7950 7740	8400
E. as in A, but 1.0N in NaOH	46.3 45.4	7800 7550	8400

† Activity of "infinitely" thick sample, corrected to standard thickness.

The existence of these phenomena call into question interpretation of the data on loss of cyanide activity as indicating a true exchange. It does not appear from the results of the present researches that exchange between any nitrile and free cyanide ion has been established.

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** The labeled sample in the form of NaC^{14}N (0.5 millicurie C^{14}) was purchased from Tracerlab, Inc., Boston, Massachusetts.

¹ P. Nahinsky, Ph.D. Dissertation, University of California, 1942.

Erratum: An Asymptotic Expression for the Energy Levels of the Asymmetric Rotor. II. Centrifugal Distortion Correction

[J. Chem. Phys. 16, 250 (1948)]

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It has been kindly pointed out by Dr. J. K. Bragg that the quantities: $\Delta\theta_0$ and $\Delta\theta'_0$, defined immediately following Eq. (3), have an incorrect sign and should be replaced by $-\Delta\theta_0$ and $-\Delta\theta'_0$, respectively.

A Further Interpretation of Interaction Terms in the Potential Function of Polyatomic Molecules

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April 22, 1949

IN recent papers¹ Duchesne and Coulson, Duchesne and Manneback have interpreted in general terms the physical meaning of the sign of the length-length and length-angle cross-terms appearing in the vibrational potential function of linear and angular triatomic molecules. In particular, they have discussed qualitatively the contribution of the interactions between non-bonded atoms on these cross-terms. Among other types of potential functions to represent those interactions, they have considered a Lennard-Jones function which they have written in the form

$$g(r_{12}) = A[m(a/r)^n - n(a/r)^m]. \quad (1)$$

In this function, A is a constant which has been supposed to be positive; a is a distance, it is in fact the distance at which the net force changes sign, m and n are 6 and 12, whereas r_{12} is the distance between the non-bonded atoms.

Using this form of potential function, it has been shown that the length-length cross-term has the expression

$$f_{12} = A \sin^2 \frac{\theta}{2} \left\{ \frac{n^2 m a^n}{r_{12}^{n+2}} - \frac{m^2 n a^m}{r_{12}^{m+2}} \right\}. \quad (2)$$

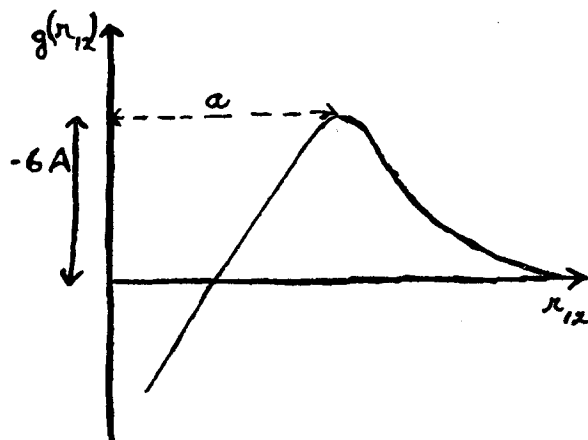


FIG. 1.

The conditions to obtain either a positive or a negative sign for f_{12} have been analysed on this basis with the result that for repulsion, f_{12} is always positive, whereas for attraction, f_{12} is generally attractive except in a small region in the neighborhood of the equilibrium position. In particular, the negative sign of f_{12} observed for HCN had been explained by an electrostatic attraction between H and N which are differently charged. It is to be remarked that the formula (2) applies to linear molecules if we put $\theta = 180^\circ$.

Until now one had not succeeded in calculating even the relative values of these cross-terms, in order to check the validity of the potential used and to try to develop a clearer basic understanding of the origin of the interactions and of the relative importance of their contributions. It is this problem that we have undertaken to deal with in this paper, using the most precise experimental data we had at our disposal for the frequencies. We will mainly confine our discussion to the symmetrical and asymmetrical linear triatomic molecules, and will reserve its extension to other kinds of molecules for a future paper.

By assuming that all the vibrations are genuinely harmonic, and applying the most general form of potential energy describing the parallel movements,

$$2V = f_1 \langle \Delta r_1 \rangle_{\text{av}}^2 + f_2 \langle \Delta r_2 \rangle_{\text{av}}^2 + 2f_{12} \Delta r_1 \Delta r_2,$$

we have calculated from the two parallel frequencies the cross-term f_{12} in cases of related molecules such as: CO_2 , CS_2 , COS , COSe , and HCN , CICN , BrCN , ICN . However, the two parallel frequencies were not sufficient to fix the exact values for the three force constants appearing for asymmetrical molecules (for the symmetrical ones $f_1 \equiv f_2$). In order to overcome this difficulty, we have assumed that the CO force constant deduced from CO_2 , remains the same in COS and in COSe , and that the CN force constant determined from HCN and DCN remains the same in CICN , BrCN , and ICN . This assumption seems very obvious since accurate values have been obtained for the interatomic distances² in those molecules from microwave measurements. It is shown indeed that the CO and the CN distances are independent of the adjacent atom within a range of at most 0.006 Å.

We summarize our results in the following Table I. We give

TABLE I.

	I				II			
f_{12}	CO_2	COS	COSe	CS_2	HCN	CICN	BrCN	ICN
	1.32	0.90	0.76	0.59	-0.30	1.014	0.956	1.07

only the value of f_{12} , which is of interest to us. It is to be noticed that the values for CO_2 , CS_2 , COS had already been calculated in recent papers¹ and that the fundamental frequencies for COSe have been kindly communicated to us by Professor Lord, to whom we are very indebted. For the series of XCN molecules we have adopted for the CN force constant the value 18.065. The values of the force constants are deduced from the fundamental frequencies and expressed in 10^5 dynes/cm units. Let us now see what happens when we suppose that the whole contribution to f_{12} arises from the interactions between the non-bonded atoms, and is represented in terms of a Lennard-Jones potential.

In the upper expression² of f_{12} , we have two unknowns A and a . Our simplifying assumption is that A is a constant which has the same numerical value for each member of a group of molecules and that a is proportional to the square root of r_{12} ($a = k\sqrt{r_{12}}$). Therefore, if we calculate A and k from f_{12} in two molecules, say from CO_2 and COS in the first group, we may predict the value of f_{12} in the others, COSe and CS_2 .

The results are summarized in Table II. It is to be noticed that A is expressed in ev.